The Southern Hemisphere Additional Ozonesondes (SHADOZ) 1998-2002 Tropical Ozone Climatology. 3. Instrumentation and Station-to-station Variability

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The Southern Hemisphere Additional Ozonesondes (SHADOZ) 1998-2002 Tropical Ozone Climatology. 3. Instrumentation and Station-to-station Variability

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Abstract: Since 1998 the Southern Hemisphere ADditional OZonesondes (SHADOZ) project has collected more than 2000 ozone profiles from a dozen tropical and subtropical sites using balloon-borne electrochemical concentration cell (ECC) ozonesondes. The data (with accompanying pressure-temperature-humidity soundings) are archived at: http://croc.gsfc.nasa.gov/shadoz. Analysis of ozonesonde imprecision within the SHADOZ dataset [Thompson et al., 2003a] revealed that variations in ozonesonde technique could lead to station-to-station biases in the measurements. In this paper imprecisions and accuracy in the SHADOZ dataset are examined in light of new data. When SHADOZ total ozone column amounts are compared to version 8 TOMS (2004 release), discrepancies between sonde and satellite datasets decline 1-2 percentage points on average, compared to version 7 TOMS. Variability among stations is evaluated using total ozone normalized to TOMS and results of laboratory tests on ozonesondes (JOSIE-2000, Jülich Ozonesonde Intercomparison Experiment). Ozone deviations from a standard instrument in the JOSIE flight simulation chamber resemble those of SHADOZ station data relative to a SHADOZ-defined climatological reference. Certain systematic variations in SHADOZ ozone profiles are accounted for by differences in solution composition, data processing and instrument (manufacturer). Instrument bias leads to a greater ozone measurement above 25 km over Nairobi and to lower total column ozone at three Pacific sites compared to other SHADOZ stations at 0-20°S.

Index Terms: 0394 - Atmos Structure & Composition - Instruments and techniques; 3309 - Climatology (Meteorology & Dynamics); Regions - 9305, 9325, 9340, 9355/Africa - Atlantic - Indian Ocean - Pacific Ocean; 3394 - Meteorology - Instruments

Free Words - Ozone, Ozonesondes, Satellite Ozone, Tropical Climatology

1. Introduction. Insights from the first three years' SHADOZ ozone data

1.1. Tropical Ozone Profiles: Needs and Status.

In the past 15 years there has been interest in enhancing the number of tropical ozone soundings because important scientific issues are hard to resolve without the vertical resolution provided through these observations. For example, there has been inadequate geographical and temporal coverage in ozone profiles for deducing ozone trends [Logan, 1994; WMO/SPARC, 1998a] in the tropics. Soundings are required to determine the vertical structure of the zonal wave-one pattern in equatorial ozone, detected by Fishman and Larsen [1987] and Shiotani [1992] with satellite data. The wave-one feature refers to more column ozone over the Atlantic and adjacent continents (with a maximum near 0° longitude) than over the Pacific with minimum ozone. Ozone profiles are also needed to evaluate satellite tropospheric ozone estimates (e.g. Fishman and Balok, 1999; Thompson and Hudson, 1999; Ziemke et al., 1998; 2002) and to suggest improved satellite retrievals.

To respond to these and other requirements, the SHADOZ project (Southern Hemisphere Additional Ozonesondes; Thompson et al., 2003a,b) was initiated to augment launches at selected tropical sites and to provide an archive of ozonesonde and radiosonde data at: http://croc.gsfc.nasa.gov/shadoz. Analysis of ~1100 ozone profiles from the 1998-2000 SHADOZ record addressed some of the issues raised above. A longitudinal cross-section of ozone showed that the wave-one is predominantly in the troposphere and occurs throughout the year [Thompson et al., 2003b]. The vertical structure of the stratospheric ozone response to the Quasi-Biennial Oscillation was detailed using balloon data within two degrees of the equator [Logan et al., 2003]. In addition, a SHADOZ campaign of opportunity, the Aerosols99 cruise on the R/V Ronald H. Brown, uncovered an "Atlantic ozone paradox" [Thompson et al., 2000], referring to a higher tropospheric ozone column over the southern hemisphere than over the northern hemisphere during the northern tropical biomass fire season. The paradox, also detected in satellite observations, appears to be a combination of cross-hemispheric transport, photochemical formation of ozone resulting from lightning-derived and pyrogenic precursors and long-range transport of southern Asian pollution interacting with convection [Edwards et al., 2003; Jenkins et al., 2003; Chatfield et al., 2004].

1.2 Ozonesonde Measurement and Impact on SHADOZ.

Besides the above insights into tropical ozone, SHADOZ soundings shed light on ozonesonde technique by providing statistics from an exceptionally large dataset. All SHADOZ stations use ECC sondes (Section 2), but variations in procedures and instrument type (there are two ECC sonde manufacturers) affect the ozone measurement [Komhyr et al., 1995; Johnson et al., 2002; Smit and Sträter, 2004a,b]. Analysis of 1998-2000 SHADOZ soundings [Thompson et al., 2003a] showed the following:

- The precision of the total ozone column by a single instrument is 5%, a value that may be better than previous evaluations [WMO, 1998a,b] because SHADOZ data are taken in a fairly uniform meteorological regime.
- Comparison with ground-based instruments at five SHADOZ stations showed agreement between integrated total ozone from the sondes ranging from 2-7% with the best agreement at Irene (South Africa) and Nairobi.
- Comparison with total ozone from the TOMS satellite (version 7 processing) indicates a
 fair degree of variability (2-11%) among stations, with the satellite measurement higher,
 on average, than the sonde total ozone.
- There is no statistically significant difference among the total stratospheric ozone column determined from SHADOZ data between 0-22°S, except for Nairobi, which is ~10 DU higher than the other stations. The Nairobi bias is greatest at the ozone maximum and

above. Ozone column amounts in the lower stratosphere (15-20 km) are the same at all SHADOZ sites (Figure 12, Thompson et al., 2003a).

• Instrument manufacturer bias, deduced from four SHADOZ stations where a mixture of instrument type had been employed, was uncertain. Two stations showed no variation. In two others, the ENSCI instrument registered several percent more ozone than the Science Pump (SPC) instrument.

Because the World Meteorological Organization (WMO) uses SHADOZ as a model for developing procedures for new stations in the Global Atmospheric Watch (GAW) program, it is important to understand possible instrument influences on the ozone profiles at individual SHADOZ stations. Chamber test experiments (JOSIE series = Jülich Ozonesonde Intercomparison Experiment) were conducted under WMO sponsorship in 1996, 1998 and 2000. In JOSIE-2000, techniques used in the SHADOZ network were intercompared through a standard ozone reference instrument. In this paper:

- Total ozone column amounts from the SHADOZ sondes are compared to version 8 (v 8) TOMS, a new processing of the satellite ozone measurement that uses SHADOZ ozone profiles. Offsets of sonde total ozone with TOMS v 8 and with colocated total ozone instruments from six SHADOZ stations are compared with the corresponding sonde and TOMS version 7 (v 7) offsets.
- Variations in total stratospheric column ozone and upper and lower stratospheric ozone columns are compared among stations to see where biases might occur.
- A SHADOZ climatological "tropical ozone profile" is used to examine variations in ozone profiles at individual sites. The latter results are compared to JOSIE chamber profiles to help interpret ozonesonde performance in SHADOZ operations.

2. Observations and Methods.

2.1 SHADOZ Data.

The SHADOZ ozonesonde measurements are made with electrochemical concentration cell (ECC) ozonesondes, in which air pumped through a cell containing a potassium iodide (KI). Sampled ozone is oxidized producing an electrical proportional to the amount of ozone in the atmosphere [Komhyr, 1967; 1986]. The signals are transmitted to a ground receiver and the ozone partial pressure is recorded through comparison with the pressure readings of an accompanying radiosonde. Designed to measure ozone concentrations from the surface to above the ozone concentration maximum, the ozonesonde-radiosonde package is flown with a balloon that usually bursts at 4-8 hPa.

SHADOZ was initiated (January 1998) with nine southern hemisphere stations and presently numbers twelve sites. Irene soundings began in late 1998 and Paramaribo, the first northern hemisphere station, started in late 1999. Launches are nominally weekly, with occasional additions during field campaigns. Experimental details are at:

http://croc.gsfc.nasa.gov/shadoz and in the Appendix of Thompson et al. [2003a]. A summary of station technique, latitude and longitude appears in Table 1.

For the present analysis, sounding data from the SHADOZ archive for 1998-2002 are used except in comparisons with TOMS where 1998-2001 data are employed. After 2001 the Earth-Probe (EP)/TOMS instrument diverged too much from the Dobson network to be reliable for our purposes [R. McPeters, personal communication, 2004].

The sonde instrument is not ideal for calculating total ozone because typically 15-20% of the ozone column is above the balloon burst, the pressure measurement of the radiosonde can become become noisy and the sampling pump rate changes. Note the following about our calculations of total ozone from SHADOZ sondes. First, no normalization is made to total ozone from another instrument, such as a satellite or a co-located ground-based total ozone sensor.

Second, only data from balloons that reached at least 10 hPa are used in computing integrated ozone. During the 1998-2000 period 75% of SHADOZ launches reached 7 hPa (analyzed in Thompson et al., 2003a). For the present analysis we choose a larger set of profiles with the 10 hPa criterion. To integrate to 1 hPa, an "evaluated ozone residual" from the SBUV satellite climatology of McPeters et al. [1997] gives an extrapolation from 10 hPa or balloon burst, whichever is higher. Extrapolation by assuming a constant mixing ratio (CMR) for ozone above balloon burst is useful for some diagnostic purposes but gives an erroneous total ozone. The third feature of SHADOZ records is that a TOMS overpass value is taken from the orbit that passes most closely to the station at roughly local noon. Most stations launch ozonesondes between 0700 and 1000 local time, so the satellite and sonde measurements are well-matched.

2.2 The Ozonesonde Measurement. JOSIE-2000.

Differences in data processing, as well as in sonde manufacturer and instrument preparation, can contribute to systematic variations among ozone measurements. Johnson et al. [2002], Thompson et al. [2003a] and Smit and Sträter [2004a,b] describe factors that may affect the ozonesonde measurement at SHADOZ sites. These include (a) the background current; (b) the concentration of potassium iodide (KI) in the cell anode and cathode; (c) strength of any buffer used; (d) the factor used to correct for the decline in pump efficiency as the sonde ascends. JOSIE experiments conducted in 1996, 1998 and 2000 suggested that these factors could be significant [WMO, 1998b; Smit and Sträter, 2004a,b], although (a) has become a more minor issue with improvements in cell manufacture. SHADOZ stations include a range of solution composition (Appendix in Thompson et al., 2003a) and at least two methods of applying the factor to correct for pump efficiency (PCF). For example, the technique at the four Pacific stations in SHADOZ is uniform and the same instrument type (SPC) is normally used. Likewise, uniform procedures are employed at Natal and Ascension (differing sensor concentration from the Pacific stations), normally with the SPC instrument.

The instrument type and sensing solution were varied in the JOSIE-2000 campaign, as shown in Tables 1 and 2. Two teams of four investigator groups participated. Each group prepared instruments for eight chamber simulations. The tests were conducted at the Forschungzentrum-Jülich environmental simulation facility [Smit et al., 2000; http://www.fz-juelich.de/icg/icg-ii/esf, established as a World Calibration Centre for Ozonesondes (WCCOS) to aid in quality assurance within the WMO/GAW network. Two tropical, two sub-tropical and two mid-latitude simulations were carried out by each group along with response time tests. Data displayed here were processed by Smit and Sträter [2004a,b]. Further details of JOSIE operations appear at the website: http://www.fz-juelich.de/icg/icg-ii/josie.

Table 2. JOSIE-2000 tests simulating SHADOZ conditions.

Test Date	Simul. No.	Condition	SHADOZ Participant
10 Sept 2000	91	Tropical	NOAA/CMDL
11 Sept 2000	92	Tropical	u
14 Sept 2000	94	Sub-tropical	u
15 Sept 2000	95	Sub-tropical	66
20 Sept 2000	98	Tropical	NASA/WFF, Meteoswiss, Univ. Réunion
21 Sept 2000	99	Tropical	

24 Sept 2000	100	Sub-tropical	46
26 Sept 2000	102	Sub-tropical	cc

3. Total Ozone: Comparison to Independent Measurements, Station Variability

Accuracy of the sonde total ozone measurement from 1998-2000 data was evaluated through comparison with total ozone measured by co-located ground-based instruments (Dobson and Brewer) at five SHADOZ sites (Figures 6 and 9 in Thompson et al, [2003a]). At each station, total ozone is also compared to the EPA/TOMS overpass total ozone column.

3.1 Total Ozone Comparisons - TOMS version 8

Figure 1 shows daily TOMS overpass data (v 8 processing, 2004 release) for 1998 through 2001 for five stations, together with total ozone integrated from the sonde (as described in Section 2) and ground-based instrument (Δ and \bullet symbols, respectively). The ground-based Dobson spectrophotometers are regularly calibrated (four sites). At Paramaribo the ozone column is based on a Brewer instrument [Peters et al., 2004]. In the lower panel, offsets among sonde, TOMS, and the ground-based instrument are shown. Total ozone comparisons similar to those in Figure 1 were depicted in Thompson et al. [2003a] using TOMS v 7 ozone.

The ozone column measurement from the sondes in Figure 1a is >5% lower in 1998-1999 compared to 2000 onward. From 1997-1999 a change in the solution composition recommended by the ENSCI manufacturer (0.5% KI compared to 1%) was employed at Natal even when the SPC sonde was flown. This is consistent with results of the JOSIE tests. During JOSIE-2000 it was shown that when the same instrument type and data processing are used, the 0.5% KI solution gives an averaged 5% lower ozone throughout the profile than does the 1% KI solution [Smit and Sträter, 2004b]. In addition to known changes in the sonde technique at Natal, there is evidence in both the colocated Dobson and Brewer instruments (the latter not shown) that TOMS ozone declined and became more variable in 2001 compared to the prior four years. Similar behavior among Brewer, Dobson and TOMS ozone was noted at Cachoeira Paulista, Brazil (23S, 38W; V. W. J. H. Kirchhoff and N. Paes Leme, unpublished manuscript, 2004).

The African stations are those with the closest agreement between TOMS and the sonde total ozone column (Figures 1b,c). This holds throughout the SHADOZ record, although the Dobson at Irene seems noisier in 1998 than later on. Both the Nairobi and Irene Dobson instruments were calibrated with the traveling world standard Dobson in Pretoria in April 2000. Data from the Nairobi Dobson are not available after that time. Judging from the sonde and Dobson, the TOMS instrument appears stable over Irene from 1998-2001. In Thompson et al. [2003a] it was noted that Irene and Nairobi are the two SHADOZ stations with elevation > 1 km. This possibly implied better agreement at sites with less tropospheric air mass because TOMS is not very sensitive below 500 hPa [Hudson et al., 1995]. However, Thompson et al. [2003a] also found (cf Figure 3 below) that much of the disagreement between TOMS total ozone and the sonde integral originates in the stratospheric part of the ozone profile. With Figure 2 showing similar TOMS-sonde offsets at Malindi (sea-level) and Nairobi (1.3 km altitude, 400 km from Malindi), there is further evidence that tropospheric discrepancies do not dominate.

At Samoa (Figure 1d) TOMS total ozone appears to be declining relative to the sonde measurement, although the early 1998 sonde data are too noisy to be definitive in this respect. There is less drift in TOMS compared to the Dobson. The tendency for the TOMS ozone column to exceed that of the Dobson by overestimating tropospheric ozone in the satellite algorithm (Figure 8c in Thompson et al., 2003b), appears unchanged in the transition from v 7 to v 8.

At Paramaribo (Figure 1e) sonde total ozone is consistently greater than the TOMS v 8

measurement and the Brewer is frequently less than the satellite ozone. In both cases, though less than three years of data are given, a TOMS downward drift is suggested in the second half of 2001. Sonde total ozone is nearly 10% higher than TOMS, on average, at that time. Paramaribo is north of the ITCZ most of the year, quite distinct from other SHADOZ stations and the ozone profile (and integrated column) may indeed diverge from them. Accordingly, in most subsequent comparisons, we do not compare Paramaribo data with the southern hemisphere data.

In Figure 2, where the TOMS-sonde total ozone differences are displayed for both v 7 and v 8 TOMS, Paramaribo shows a negative deviation. Figure 2 also shows a tendency for the Pacific SHADOZ stations and Watukosek to be biased lower relative to TOMS than the Atlantic and African stations. One reason for this is that the TOMS algorithm (both versions 7 and 8) assumes a greater tropospheric ozone column depth (29.8 DU; Table 4 in Thompson et al., 2003b) than actually measured at the Pacific stations (mean tropospheric column depth, ~19 DU). There is only a 1-2 percentage point change to the TOMS-normalized data at the SHADOZ stations (Table 3) using v 8 compared to v 7. However, agreement between the southern hemisphere Dobson stations and TOMS v 8, spanned within the shading in Figure 2, improved over v 7 (compare offsets shown in [Bodeker et al., 2001]).

3.2 Stratospheric Ozone Comparisons from SHADOZ Sondes

We also examined the integrated stratospheric ozone column to see whether some of the SHADOZ station variability is due to stratospheric ozone variability among the sites (refer to Figures 10-12 in Thompson et al. [2003a]). These analyses are performed with the 1998-2002 sondes in three ways, as illustrated in Figures 3a-c. The total integrated stratospheric ozone column in Figure 3a includes the measured ozone column to 10 hPa and the SBUV extrapolation. The latter quantity is an average by month and latitude band, i.e., 0-10N, 0-10S, 10-20S [McPeters et al., 1997]. The range of SBUV extrapolation values used for 10-1 hPa is 36-48 DU. Figure 3a, which presents the total integrated stratospheric ozone column (± 1-\sigma), shows all the stations overlapping except for Ascension Island (lowest at 167 DU) and Paramaribo (highest at 196 DU). All other SHADOZ stations are within the range 177-192 DU. In Thompson et al. [2003a] it was concluded that the SHADOZ record does not show a statistically significant stratospheric wave-one pattern. Additional data in the present analysis (~40% more profiles than in Thompson et al. [2003a]) lead to the same conclusion.

Two diagnostics are used to look more closely at stratospheric variability: the 15-20 km integral (~110-60 hPa) and the CMR extrapolation. Figure 3b, depicting the lower stratospheric integrated ozone column, shows almost no variation among the SHADOZ stations (compare Figure 11 in Thompson et al. [2003a], where 1998-2000 data were used). An exception is Irene, where roughly half the observations are made at mid-latitude conditions. Not counting Irene, the range of mean 15-20 km ozone column is ~4 DU. The 15-20 km ozone column uniformity is taken as further evidence for the lack of a stratospheric wave because zonal variation is expected in the lower stratosphere [Shiotani and Hasebe, 1994; Newchurch et al., 2001].

The CMR is used to diagnose the relative behavior of the upper stratosphere which is not expected to vary among the southern hemisphere SHADOZ sites. In Figure 3c, raw CMR values are not displayed but rather their deviation from the SBUV add-on for each station (Table 2). Variations in the CMR-SBUV parameter may reflect the effect of the sensing solution, the instrument used or data processing (primarily the PCF employed by each station Co-Investigator). Here, in contrast to the lower stratosphere bias (Figure 3b), the range across the SHADOZ stations exceeds 10 DU. The Atlantic stations (Paramaribo-Natal-Ascension) are relatively high whereas for total stratospheric ozone, Natal and Ascension are relatively low (Figure 3a). Irene, Fiji and San Cristobal are the lowest in normalized CMR. Can the precision

of the stratospheric quantities be estimated using the CMR normalized statistics? The Natal-Ascension pair and Fiji-Samoa pair are only 4 DU apart. Nairobi and Malindi, stations ~400 km apart, are within 2 DU of one another in all three stratospheric analyses shown in Figure 3.

3.3 Implications of JOSIE-2000 for SHADOZ Total and Stratospheric Ozone

How do we interpret some of the apparent systematic differences among SHADOZ stations? The possibility of instrument effects is considered by referring to selected JOSE-2000 results. First, the deviation between integrated ozone from the sonde in the chamber relative to the ozone photometric (OPM) standard is compared to normalized total ozone from SHADOZ sites. In other words, TOMS, the ground-based instruments and the OPM are treated as standards through which the sonde ozone total is intercompared. Figure 4 depicts the following:

- Ozone data from the test chamber integrated from surface conditions to 10 hPa using the
 appropriate instrument type for a given SHADOZ station differenced with the integrated
 ozone from the JOSIE-2000 OPM. The chamber ozone column was computed with the
 participant's own pump correction factor to capture possible processing biases as well as
 effects of instrument type and sensing solution.
- Ozone integrated from the SHADOZ station sondes relative to TOMS total ozone from satellite overpasses (as in Figure 2).
- Total column ozone from ground-based instruments at five SHADOZ stations (four Dobsons, one Brewer) differenced to the TOMS overpass total ozone.

Figure 4 shows that differences between sonde total ozone from the three Pacific stations and Watukosek and v 8 TOMS (with the sonde reading low relative to the satellite) are mostly consistent with the JOSIE-2000 results. The field instruments (SPC) read ~7% lower than TOMS at Samoa and Fiji. That is nearly identical to the JOSIE deviation from the OPM and within 2% of the TOMS-sonde offsets at Watukosek, where the same technique (NOAA/CMDL method) is used. The TOMS-sonde agreement at San Cristóbal is similar to Samoa and Watukosek but the TOMS-sonde discrepancy is slightly worse than the JOSIE sonde-OPM disagreement. Dobson-TOMS (Samoa) and Brewer-TOMS (Watukosek) offsets are smaller (2% absolute) than the sonde-TOMS offsets for these stations and for San Cristóbal and Fiji.

Natal shows close agreement between the sonde-TOMS discrepancy (Figure 4) and the JOSIE-2000 chamber tests, where the sonde ozone total was ~2.5% lower than the standard. The Dobson, however, was ~2.5% higher than TOMS ozone at Natal. Also, in Figure 4, JOSIE-2000 tests show the instrument type (ENSCI) reading greater in total ozone than the OPM standard for the Réunion and Meteoswiss (Nairobi) participants. The sondes recorded 6-7% greater ozone than the reference. For the corresponding SHADOZ measurements at Nairobi, total ozone normalized to TOMS reads higher than at all other stations but one (Malinidi). However, the TOMS-sonde offset at Nairobi is less than the bias of the corresponding JOSIE instruments. The TOMS-sonde offset based on Réunion measurements differs nearly 10% from the chamber tests.

4. SHADOZ Ozone Profile Analysis

Although there are relatively small differences in stratospheric ozone column among SHADOZ stations, it is important to evaluate variability arising from the ozone measurement in various parts of the profile. This is done in two steps. First, mean SHADOZ ozone profiles from each station are compared to an overall mean SHADOZ profile. Second, biases in the stratospheric ozone segments at SHADOZ stations are compared to corresponding behavior of the station technique as tested in JOSIE-2000.

4.1 Characteristics of Mean SHADOZ Profiles

Figure 5 shows the mean profile from each southern hemisphere SHADOZ station. The CMR isolines are drawn to show tendencies for upper stratospheric variability among the SHADOZ stations. What is observed? For the three Pacific stations and Watukosek (Figure 5a).

ozone profiles are nearly identical in the lower stratosphere but there is divergence at the stratospheric maximum. For Watukosek the maximum occurs at ~15 hPa and the corresponding partial pressure is 14 mPa. For Fiji the maximum partial pressure is ~13mPa. Extrapolations above 7 hPa (the minimum pressure plotted) fall between the 8 and 10 ppmv isolines. The tropospheric profiles of the three Pacific stations are similar in integrated column amount and shape. At the surface, ozone is < 2 mPa (14.5 ppbv), declining to the top of the mixed layer. Ozone then increases to ~600 hPa where a second decline begins that continues to the tropopause. The lower tropospheric layer of maximum ozone is due to imported pollution. Only at Watukosek, among SHADOZ sites, does pollution-level ozone occur at the surface.

Figure 5b shows that the two Atlantic and two Kenyan stations are similar in the stratosphere (~ 15 mPa at maximum) except for Ascension where the maximum partial pressure is < 14hPa. The upper stratosphere ozone (signified by CMR isoline at 12 ppmv) for Natal, Nairobi and Malindi is also greater than for Ascension. In the troposphere, Natal and Ascension have peak ozone partial pressure at 700 hPa, a consequence of long-range transport of pollution. Back-trajectories initialized at 700 hPa from Natal and Ascension on days of ozonesonde launch (images available at the SHADOZ website) show African origins for the highest ozone episodes. The two sub-tropical SHADOZ stations (Figure 5c) have peak ozone partial pressure closer to 30 hPa than to 20 hPa (compare the tropical maximum in Figures 5a,b). Sub-tropical profiles are signified by more ozone throughout the lower stratosphere and upper troposphere. In the uppermost stratosphere, Irene and Réunion differ, with the latter always higher. This causes a 5 DU difference in the normalized CMR between the two stations (Figure 3c).

For purposes of examining relative features of individual station profiles, it is useful to define "mean tropical" and "mean sub-tropical" ozone profiles from SHADOZ data. These can be viewed as analogous to the JOSIE-2000 OPM "standard" tropical and sub-tropical profiles. A SHADOZ "mean tropical" ozone profile, with 1- σ standard deviation (Figure 6a), is based on the eight stations illustrated in Figures 5a and 5b plus 1998-1999 statistics from Tahiti (see Table 3 in Thompson et al. [2003a]). For Watukosek, only data from after July 1999, when soundings with ECC instruments were initiated, appear in the average. Likewise, the Réunion (21°S) and Irene (26°S) ozone data are used to define a SHADOZ "mean sub-tropical" ozone profile (Figure 6b.) The integrated ozone column amounts show a tropical-sub-tropical difference of ~15 DU: Integrated ozone, surface--10 hPa: 189.4 DU, tropical 206.1 DU, sub-tropical Integrated ozone, surface--7 hPa: 212.5 DU, tropical 225.4 DU, sub-tropical

4.2 SHADOZ Ozone Profile Climatologies Relative to Means

In Figure 7a-h individual station ozone profiles, normalized to the SHADOZ tropical mean, are depicted. Positive deviations signify a higher bias at the same pressure at a SHADOZ station relative to the climatological ozone value. Tropospheric absolute deviations sometimes exceed 40%. In the stratosphere (taken as above 100 hPa for convenience), the deviations rarely exceed 10%. On average, above 70 hPa, Samoa (Figure 7a) is closest to the climatological mean with absolute deviation < 5% up to 10 hPa. Above 80 hPa San Cristóbal (Figure 7b) is also close to the climatology and the shape is quite uniform throughout the stratosphere. Fiji is distinctive among the stations illustrated (Figure 7c) in having the largest positive deviation in the lower stratosphere between 40 and 95 hPa. Ascension and Natal (Figures 7d,e) parallel one another in the stratosphere. There is a monotonic change in the deviation, starting from station sondes biased low relative to climatology. At 10 hPa, both are within 5% of the mean ozone value and 5-10% greater than Samoa, San Cristobal and Fiji at 10 hPa. Nairobi deviations (Figure 7f) resemble Ascension and Natal throughout most of the stratosphere. An exception is in the 80-60 hPa range where the Nairobi sondes are greater than climatology by ~5% and Ascension and Natal (Figures 7 d,e) are low by 5-10%. Malindi (Figure 7g) has positive deviations throughout

the stratosphere, similar to Nairobi (Figure 7f). Watukosek (Figure 7h) has the greatest deviation from the mean at the 100 hPa level but above 60 hPa is always within 5% of the mean.

The results shown in Figure 7 are explored further to see if the tendencies recorded in ozone above 100 hPa are consistent with the total ozone patterns and with independent evaluation of the SHADOZ technique. First we ask: (1) How do the profile deviations from a SHADOZ tropical climatology (depicted in Figure 7) compare to variability in total ozone from among the stations? The information summarized in Figure 7 is compared to Figure 3 and Table 3. Figure 3 showed that column-integrated stratospheric ozone to 10 hPa at Samoa, San Cristóbal, Watukosek and Fiji fall within a 7 DU (177-184 DU) range of one another. This is consistent with Samoa and San Cristóbal having profiles close to the tropical mean (Figures 7a,b). The deviations within the Fiji profile (Figure 7c), positive above 30 hPa and negative below, apparently cancel out in the stratospheric integral. Table 3 (also Figure 3a) shows the Fiji stratospheric column (179.7 DU) close to the all-southern tropical station mean (181.8 DU).

Figure 3 and Table 3 show Ascension ~10 DU less in stratospheric column than the other stations whereas Nairobi and Malindi are ~10 DU greater. Figure 7 indicates how these variations might come about. The Ascension stratospheric profile (Figure 7d) is 5% lower than climatology, on average, throughout the stratosphere. However, at 80-100 hPa, Ascension is greater than climatology so the 15-20 km column integral (Figure 3b) does not deviate significantly from the other stations. Natal (Figure 7e), like Fiji, has deviations both positive and negative so that its stratospheric integral falls near the mean (Figure 3a). Nairobi and Malindi (Figures 7f,g) are roughly 5% higher than the climatological profile throughout the stratosphere.

4.3 SHADOZ Profile Biases and JOSIE-2000 Results

How do the deviations at individual SHADOZ stations, relative to the tropical climatology, compare to profile deviations for the given technique as recorded in the JOSIE-2000 tests with a reference ozone standard? Figure 8 illustrates the stratospheric offsets from the SHADOZ climatology (as in Figure 7) along with deviations between the corresponding chamber instrument and the JOSIE OPM. The latter deviations plotted are based on the participants specified corrections (PSC). Figure 7 in Johnson et al. [2002] shows that the PSC adds 5-10% to the measured value above 100 hPa for all but one method used in SHADOZ (Table 1; see also Table A-1 in Thompson et al. [2003a]). The exception is a higher PSC (up to 20% added) used where the NOAA/CMDL technique is employed (four Pacific stations and Watukosek after July 1999).

Comparisons are given for three instrument types: NOAA/CMDL method (Samoa, Fiji, San Cristóbal, Figures 8 a,b); NASA/WFF method with Natal and Ascension (Figures 8 c,d); the Meteoswiss method with Nairobi (Figures 8e,f). Figures 8a and 8b represent two tropical JOSIE-2000 simulations and display, respectively, the deviations of the sonde from the OPM standard with the NOAA/CMDL sensing solution (2% KI, no buffer) in cells of SPC and ENSCI manufacture. The NOAA/CMDL method is low (~50%) compared to the OPM at 100 hPa. As the pressure falls below 60 hPa, agreement improves to within 10% of the standard, averaging a little below the OPM in Figure 8a (the SPC instrument) and a little above the OPM (ENSCI) in Figure 8b. For the NASA/WFF (Figure 8c,d) and Meteoswiss (Figure 8e,f) methods, JOSIE-2000 also shows an underestimate of ozone relative to the OPM in the 100-60 hPa range, though of less magnitude (10-20% deviation) than the NOAA/CMDL method. Deviations of NASA/WFF JOSIE and SHADOZ Natal sondes minimize at 40 hPa (Figure 8c,d).

In Figure 8 the low-ozone bias in all cases in the 100-60 hPa region in the JOSIE-2000 tests reflects the very low absolute ozone amount at 100 hPa in the simulated profile. The sonde responses, determined in pre-experiment tests (or pre-launch, in the field), are typically 22-35 seconds, whereas the photometer senses an ozone change within a second. In the chamber

simulation, the ozone partial pressure was nearly zero from 180-100 hPa. Above 100 hPa, as in the tropical atmosphere, ozone increases sharply but the sondes never respond as quickly as the photometer. As ozone continues to increase with decreasing pressure, the percentage lag is less; the agreement with the OPM improves.

Differences among sonde performance in the JOSIE-2000 stratospheric simulations also reflect variations in the sonde sensing solution and ECC instrument type. The large contrast in sonde response in the 100-60 hPa range when the NOAA/CMDL method (Figure 8a,b) is compared to the other two methods (Figures 8c-f) stems from a difference in buffering of the KI solution. After a strong ozone signal has been measured, a buffered solution responds to lower ozone sluggishly, a "memory" effect. The unbuffered NOAA/CMDL solution (Figure 8 a,b) appears to have a greater lag in the 100-60 hPa region relative to the NASA/WFF and Meteoswiss instruments (with buffered solutions) because there is no memory from previous measurements. Thus, the apparent better ozone response of the NASA/WFF and Meteoswiss instruments in the lower stratosphere, either simulated or when Fiji offsets (Figure 8a,b) are compared to Natal or Nairobi (Figures 8c-f), for example, is partly an artifact of the solution.

The impact of buffering may be significant in the upper stratospheric portion of the ozone profile (40-10 hPa in Figure 8) where the ozone maximum occurs. However, this influence is more difficult to gauge because PSCs are included in both the JOSIE-2000 and SHADOZ data. In the case of the NOAA/CMDL method (Figure 8a,b) the JOSIE-2000 tests show a slight positive bias above 20 hPa but the SHADOZ data are all relatively low compared to the tropical climatology. Fiji, Samoa, San Cristóbal ozone deviations (Figure 8a,b) average ~15% lower than ozone at Nairobi above 20 hPa (Figure 8e,f) and 5-10% lower than Natal (Figure c,d).

The Meteoswiss JOSIE-2000 results and SHADOZ Nairobi sonde deviations (Figure 8e,f) generally follow one another. The Nairobi sondes are higher than the SHADOZ climatology throughout the stratosphere. The JOSIE-2000 tests showed a mostly positive bias for the Meteoswiss method above 65 hPa. The Meteoswiss and NASA/WFF results appear to illustrate a difference in instrument type. The JOSIE readings shown in Figures 8c-f were taken during the same chamber simulations (Nos. 98 and 99) with identically prepared sensing solution. Relative to the OPM, the raw signal recorded with the Meteoswiss ENSCI instruments measured 5-10% more ozone throughout the simulated stratosphere than NASA/WFF with SPC. This is equivalent to an integrated ozone difference of ~20 DU, similar to the high-bias depicted for Nairobi in Figure 3a. These contrasts resemble those of the Nairobi sondes relative to the SHADOZ tropical climatology and to the Natal and Ascension offsets above ~85 hPa (compare Figures 8c and 8e). The tendency for the ENSCI instrument to record 5-7% more total ozone from 100-10 hPa than the SPC when the same solution composition and processing are employed, was a major finding of JOSIE-1998 and JOSIE-2000 [Smit and Sträter, 2004a,b]. The same behavior is observed when ENSCI and SPC instruments prepared identically are launched on the same balloon [Johnson et al., 2002; F. J. Schmidlin, personal communication, 2003]. The high ENSCI bias may explain why Watukosek is higher in the upper stratosphere than similarly prepared sondes at the three Pacific stations where the SPC instrument is used (Figure 5a)

5. Summary

In the first part of this paper total ozone columns from SHADOZ stations are compared to the new v 8 TOMS total ozone product for the period 1998-2001. At five SHADOZ sites, comparisons are also made with ground-based instruments that measure total ozone. The results can be summarized as follows:

1. Comparison of total ozone from the SHADOZ sondes and v 8 TOMS shows that, on average, the satellite records greater ozone column amount than the sondes or co-located Dobson instruments. An exception is at Paramaribo, where the sonde total ozone is more

- than 5% greater than the satellite overpass amount. These results are similar to sonde comparisons with v 7 TOMS [Thompson et al., 2003a] but there is a 1-2% improvement in agreement between the sonde ozone and v 8 TOMS due to re-calibration of TOMS.
- 2. Station-to-station total column differences between sonde and TOMS v 8 ozone, averaged from 1998-2001, are similar to those for 1998-2000 based on comparisons with TOMS version 7 [Thompson et al., 2003a]. Also similar to v 7, the worst agreement between TOMS v8 and the southern hemisphere sondes occurs at stations with the lowest tropospheric column ozone.
- 3. Evaluation of column ozone segments within the stratosphere, based on 1998-2002 SHADOZ data, shows the same stratospheric uniformity (no longitudinal wave-one) and upper stratospheric biases reported by Thompson et al. [2003a].

In the second part of our analysis, variability among SHADOZ stations, normalized to a climatological profile, is evaluated through comparison with instrument performance in JOSIE-2000 chamber simulations of balloon ascents in a tropical regime. The major findings include:

- 4. Nairobi sondes from SHADOZ show a high-ozone bias throughout the stratosphere relative to the other southern hemisphere station data. As a result, the mean stratospheric ozone column amount over Nairobi is ~15 DU higher.
- 5. The JOSIE-2000 chamber tests suggest that the high-ozone bias at Nairobi can be explained by a combination of the instrument type and sensing solution employed by the Meteoswiss-Kenya Meteorological Department. Above the 20-km mark in the JOSIE chamber, the Meteoswiss (ENSCI) instrument read 5-10% higher than the NASA/WFF instrument (SPC) that used the same solution type. Similar contrasts occur in normalized Nairobi and Ascension/Natal ozone profiles.
- 6. In JOSIE-2000 too low ozone was measured in lower stratospheric segments (100-60 hPa) where sonde responses lag the standard photometer by 20-30 seconds. This effect appears in segments of four SHADOZ stations (Ascension, Natal, Samoa, San Cristóbal).
- 7. The impact of sensing solution composition on SHADOZ station variability is harder to assess because PSCs are included in the archived data. JOSIE-2000 results show memory effects associated with buffered solutions (used at all sites except those with the NOAA/CMDL method), especially in the lowest ozone segments (~100 hPa). The memory effects may also explain positive offsets above 20 hPa at Nairobi and Natal. At Fiji, Samoa and San Cristóbal, where unbuffered solutions are used, upper stratospheric ozone profiles are lower than the SHADOZ-defined climatology.

Bearing in mind that SHADOZ statistics represent hundreds of balloon flights at some stations, compared to a small number of simulations in the JOSIE-2000 test chamber (two prototype profiles/technique), it is gratifying to note that sonde deviations in JOSIE are roughly reflected in the sonde biases within the SHADOZ dataset. Ozonesonde instrument issues will be further evaluated with results from an April 2004 balloon intercomparison called BESOS (Balloon Experiment for Standards of Ozonesondes; http://croc.gsfc.nasa.gov/besos). As in the JOSIE experiments, BESOS features a standard ozone photometer through which a set of sondes flown on the same gondola are intercompared (cf Hilsenrath et al., 1986).

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Table 1. SHADOZ sites, instrument technique, parameters during JOSIE-2000 tests.

SHADOZ Sites	Lat./Long	. (deg)	Station Meth.	Station Instru.	JOSIE Meth.*	JOSIE Instru.
Suva, Fiji	-18.13	178.40	2% KI	SPC	2% KI	SPC
Pago Pago, Am. Samoa	-14.23	-170.56	2% KI	SPC	2% KI	SPC
Papeete, Tahiti	-18.00	-149.00	2% KI	SPC	2% KI	SPC
San Cristóbal, Galapagos	-0.92	-89.60	2% KI	SPC	2% KI	SPC
Paramaribo, Surinam	5.81	-55.2	1% KI	SPC		
Natal, Brazil	-5.42	-35.38	1% KI	SPC,** ENSCI	1% KI	SPC
Ascension Island	-7.98	-14.42	1% KI	SPC,** ENSCI	1% KI	SPC
Irene, South Africa	-25.25.	28.22	1% KI	SPC		
Nairobi, Kenya	-1.27	36.80	1% KI	ENSCI	1% KI	ENSCI
Malindi, Kenya	-2.99	40.19	1% KI	SPC		
La Réunion	-21.06	55.48	.5, 1% KI	SPC,** ENSCI	.5, 2% KI	ENSCI
Watukosek, Indonesia	-7.57	112.65	1%?	ENSCI		****
Kaashidhoo, Maldivest	5.0	73.5	2% KI	ENSCI	_	
Aerosols99 Cruiset			2% KI	ENSCI	_	

^{*} Responsible Co-I JOSIE participant: NOAA/CMDL for Fiji, Samoa, San Cristobal, Tahiti; NASA Wallops Flight Facility (WFF) for Natal, Ascension; Méteosuisse for Nairobi; Univ. Réunion for La Réunion. FZ-Juelich JOSIE participant test method used at Irene, Paramaribo.

^{**} Mixture of solution strengths, instruments used; see details in Thompson et al. [2003a]

[†] Campaign data in SHADOZ archive. 23 sondes from Aerosols99 cruise, January-February 1999 [Thompson et al., 2000]; 54 sondes from Kaashidhoo taken during late January-March 1999 [Figure 11b in Thompson et al., 2003b]

Table 3. Ozone summary from 1998-2002 SHADOZ data. Total sample number given along with the number of profiles to 10 hPa, on which

Cite	3					-			
alic	Sample No. /total profiles	Integrated O ₃ ,	Trop O ₃ , 1σ	Int. O ₃ -Trop O ₃ , 1σ	CMR Add-on, 10	SBUV Add- on, 10	Total Sonde O ₃ + CMR, 10	Total Sonde O ₃ + SBUV,	(CMR- SBUV), 10
Ascension	164/222	204.3, 21.4	37.0.89	1673 162	26.2.12.0	1 7 67		10	
:: [101.05.10.4	00.2, 12.0	48.4, 7.7	270.4, 25.5	252.7, 19.7	17.7, 8.3
riji	151/181	202.1, 15.8	22.4, 7.5	179.7, 12.0	50.1, 8.7	38.6.64	2523 168	240 0 14 0	
Irene	100/123	224 0 20 1	33.1.60	1			2,22,10.3	240.8, 14.8	11.5, 5.2
		100 601	33.1, 0.0	190.9, 17.9	50.0, 10.0	39.9, 7.1	274.0, 22.6	263.9, 19.4	10.2 5.9
Watokusek	82/140	208.4, 16.7	24.4, 7.2	184.0, 14.3	55.1, 11.8	37767	763 4 22 3		600 (200)
Malindi	15157	010 200				27.1,90.7	203.4, 22.3	246.1, 14.3	17.3, 10.6
TATIGUE	42/0/	219.6, 32.3	32.4, 6.3	191.6, 12.6	57.5, 14.0	38.1.7.6	277 1 30 3	257 9 27 0	, , ,
Nairobi	193/231	221.6.14.4	18861	1007 104			6.66.	637.6, 32.0	19.3, 9.4
			1000	172.7, 12.4	59.4, 10.3	39.3, 6.8	281.0, 14.4	260.9, 12.3	20 1 5 9
Natal	150/177	214.3, 17.4	32.9, 8.5	181.4, 13.7	65.1, 12.1	44 0 7 8	370 1 22 0	250 2 122	7.0
Paramaribo	125/156	236.0. 15.8	30 8 87 0	106.3.00.0			617.7, 44.0	236.3, 17.3	21.1, 8.4
			0.70	7.90,5,06.7	64.9, 11.6	40.9, 7.0	300.9, 18.0	276.9, 13.4	24.0, 8.1
Keunion	95/149	210.0, 17.7	32.8, 7.4	177.1, 14.1	56.6, 10.9	43 1 8 1	366 6 20 0		
Samoa	162/104	201 0 100				10.1,0.1	400.0, 40.0	253.1, 15.5	13.5, 8.5
	102/134	201.0, 12.9	19.8, 5.9	181.2, 9.8	51.0, 8.3	36.1, 4.5	252.0. 15.0	237 1 12 3	140 67
San Cristobal	191/217	200.4, 14.3	23.6, 4.5	176.8, 12.3	49395	37.3 6.0	270 11000		14.6, 3.7
					27, 62,7	0.0,000	249.7, 16.3	237.7, 12.7	12.0, 6.9

calibration performed by the station Co-Investigator, who may re-process at any time. Updates (with most recent processing date) are given on the Total samples used in statistical analyses (first column): 1458. The SHADOZ project archives data in a uniform format, with initial analysis and website. Some sites report data every 10 seconds during a flight, whereas other profiles are archived with 1-s frequency. Data from SHADOZ stations maintained at other archives may differ from SHADOZ in format, ozone integration and extrapolation.

REFERENCES

- Bodeker, G. E., J. C. Scott, K. Kreher, and R. L. McKenzie, Global ozone trends in potential vorticity coordinates using TOMS and GOME intercompared against the Dobson network: 1978-1998, J. Geophys. Res., 106, 23029-23042, 2001.
- Chatfield, R. B., H. Guan, A. M. Thompson, and J. C. Witte, Convective lofting links Indian Ocean air pollution to paradoxical south Atlantic ozone maxima, *Geophys. Res. Lett.*, 31, L06103, doi: 10.129/2003GL016688, 2004.
- Edwards, D. P., et al., Tropospheric ozone over the Atlantic: A satellite perspective, J. Geophys. Res., 108, 4237, doi: 10.129/2002JD002927, 2003.
- Fishman, J. and A. Balok, Calculation of daily tropospheric ozone residuals using TOMS and empirically improved SBUV measurements: Application to an ozone pollution episode over the eastern United States, J. Geophys. Res., 104, 30319-30340, 1999.
- Fishman, J., and J. C. Larsen, Distribution of total ozone and stratospheric ozone in the tropics Implications for the distribution of tropospheric ozone, J. Geophys. Res., 92, 6627-6634, 1987.
- Hilsenrath, E., et al., Results from the Balloon Ozone Intercomparison Campaign (BOIC), J. Geophys. Res., 91, 13137-13152, 1986.
- Hudson, R. D., J. Kim, and A. M. Thompson, On the derivation of tropospheric column ozone from radiances measured by the Total Ozone Mapping Spectrometer, J. Geophys. Res., 100, 11138-11145, 1995.
- Jenkins, G. S., J-H. Ryu, A. M. Thompson, J. C. Witte, Linking horizontal and vertical transport of biomass fire emissions to the tropical Atlantic ozone paradox during the Northern Hemisphere winter season. 1999, J. Geophys. Res., 108, 4745, doi:10.129/2002JD003297, 2003.
- Johnson, B. J., S. J. Oltmans, H. Vömel, T. Deshler, C. Kroger and H. G. J. Smit, ECC ozonesonde pump efficiency measurements and sensitivity tests of buffered and unbuffered sensor solutions, J. Geophys. Res. 107, D19, 4393, doi: 10.129/2001JD000557, 2002.
- Komhyr, W. D., Nonreactive gas sampling pump, Rev. Sci. Inst., 38, 981-983, 1967.
- Komhyr, W. D., Operations Handbook Ozone measurements to 40 km altitude with model 4A-ECC-ozone sondes, NOAA Techn. Memorandum ERL-ARL-149, 1986.
- Komhyr, W. D., R. A. Barnes, G. B. Brothers, J. A. Lathrop, and D. P. Opperman, Electrochemical concentration cell ozonesonde performance during STOIC, *J. Geophys. Res.*, 100, 9231-9244, 1995.
- Logan, J.A., Trends in the vertical distribution of ozone: An analysis of ozone sonde data, J. Geophys. Res., 99, 25553 25585, 1994.
- Logan, J. A., D. B. A. Jones, I. A. Megretskaia, W. Randel, S. J. Oltmans, B. J. Johnson, H. Voemel, W. Kimani, and F. J. Schmidlin, The quasi-biennial oscillation in equatorial ozone as revealed by ozonesonde and satellite data, J. Geophys. Res., 108, doi: 10.129/2002JD002170, 2003.
- McPeters, R. D., G. J. Labow and B. J. Johnson, A satellite-derived ozone climatology for balloonsonde estimation of total column ozone, *J. Geophys. Res.*, 102, 8875-8885, 1997.
- Newchurch, M. J., D. Sun and J-J. Kim, Zonal wave-1 structure in TOMS tropical stratospheric ozone, Geophys. Res. Lett., 28, 3151-3154, 2001.
- Peters, W., M. C. Krol, J. P. F. Fortuin, H. M. Kelder, C. R. Becker, A. M. Thompson, J. Lelieveld, P. J. Crutzen, Tropospheric ozone over a tropical Atlantic station in the northern hemisphere: Paramaribo, Surinam (6N, 55W), Tellus B, 56, 21-34, 2004.
- Shiotani, M. Annual, quasi-biennial and El Nino-Southern Oscillation (ENSO) time-scale variations in Equatorial total ozone, J. Geophys. Res., 97, 7625-7634, 1992.
- Shiotani, M., and F. Hasebe, Stratospheric ozone variations in the equatorial region as seen in Stratospheric Aerosol and Gas Experiment data, J. Geophys. Res., 99, 14575-14584, 1994.
- Smit, H. G. J., W. Sträter, M. Helten, and D. Kley, Environmental simulation facility to calibrate airborne ozone and humidity sensors, Jülich Berichte Nr 3796, Forschungszentrum Jülich, 2000.
- Smit, H. G. J., and W. Sträter, JOSIE-1998: Performance of ECC Ozone Sondes of SPC-6A and ENSCI-A Type, in WMO Global Atmospheric Watch Report Series (Technical Document), World Meteorological Organization, Geneva, in press, 2004a.
- Smit, H. G. J., and W. Sträter, JOSIE-2000: The 2000 WMO international intercomparison of operating procedures for ECC-sondes at the environmental simulation facility at Jülich, in WMO Global Atmospheric Watch Report Series (Technical Document), World Meteorological Organization, Geneva, in press, 2004b.
- Thompson, A. M. and R. D. Hudson, Tropical tropospheric ozone (TTO) Maps from Nimbus 7 and Earth-Probe TOMS by the modified-residual method: Evaluation with sondes, ENSO signals and trends from Atlantic regional time series, J. Geophys. Res., 104, 26961-26975, 1999.
- Thompson, A. M., B. G. Doddridge, J. C. Witte, R. D. Hudson, W. T. Luke, J. E. Johnson, B. J. Johnson, S. J. Oltmans, and R. Weller, A tropical Atlantic ozone paradox: Shipboard and satellite views of a tropospheric ozone

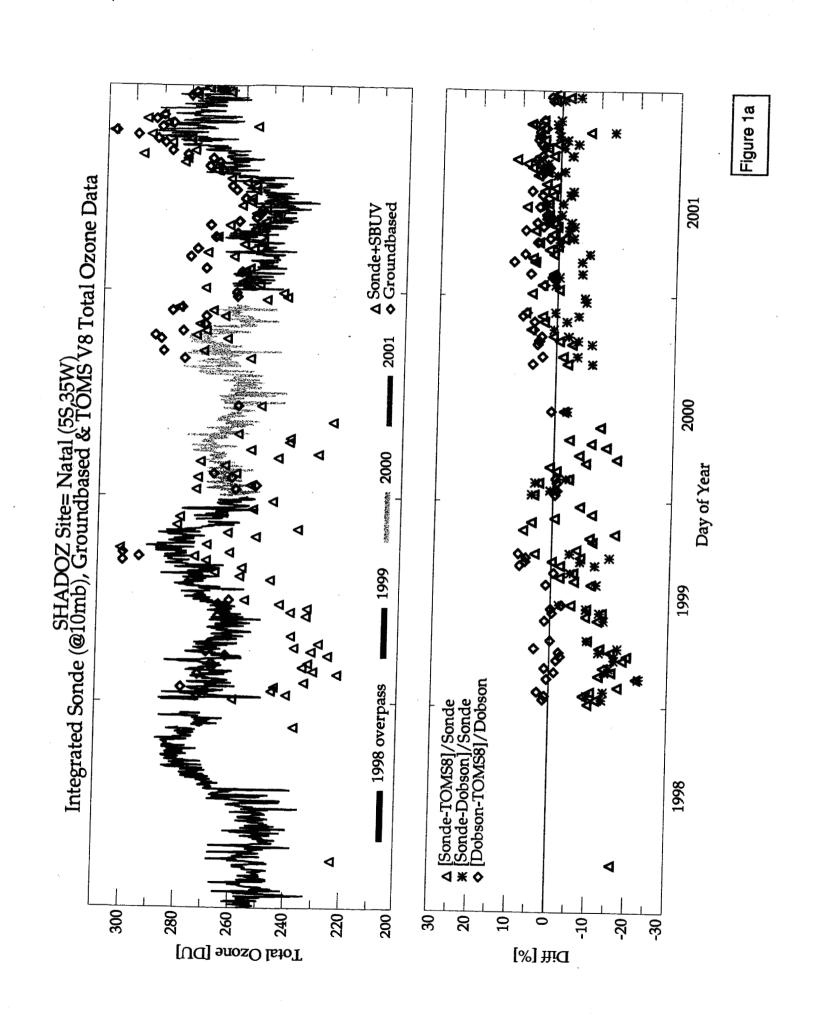
- maximum and wave-one in January-February 1999, Geophys. Res. Lett., 27, 3317-3320, 2000.
- Thompson, A. M., et al., Southern Hemisphere Additional Ozonesondes (SHADOZ) 1998-2000 tropical ozone climatology. 1. Comparison with TOMS and ground-based measurements, J. Geophys. Res., 108, D2, 8238, doi: 10.129/2001JD000967, 2003a.
- Thompson, A. M., et al., Southern Hemisphere Additional Ozonesondes (SHADOZ) 1998-2000 tropical ozone climatology. 2. Tropospheric ozone variability and the zonal wave-one, *J. Geophys. Res.*, **108**, D2, 8241, doi: 10.129/2002JD002241, 2003b.
- WMO (World Meteorological Organization), SPARC/IOC/GAW Assessment of Trends in the Vertical Distribution of Ozone, ed. By N. Harris, R. Hudson and C. Phillips, SPARC Report No. 1, WMO Global Ozone Research and Monitoring Project, Report No. 43, Geneva, 1998a.
- WMO (World Meteorological Organization), JOSIE, ed. by H. Smit and D. Kley, Report No. 130, WMO Global Ozone Research and Monitoring Project, Report No. TD926, Geneva, 1998b.
- Ziemke, J. R., S. Chandra, and P. K. Bhartia, Two new methods for deriving tropospheric column ozone from TOMS measurements: The assimilated UARS MLS/HALOE and convective-cloud differential techniques, J. Geophys. Res., 103, 22115-22128, 1998.
- Ziemke, J. R., S. Chandra, and P. K. Bhartia, Upper tropospheric ozone derived from the cloud slicing technique: Identification of the regional aspects of air pollution, J. Geophys. Res., 108, 4390, doi: 10.129/, 2002.

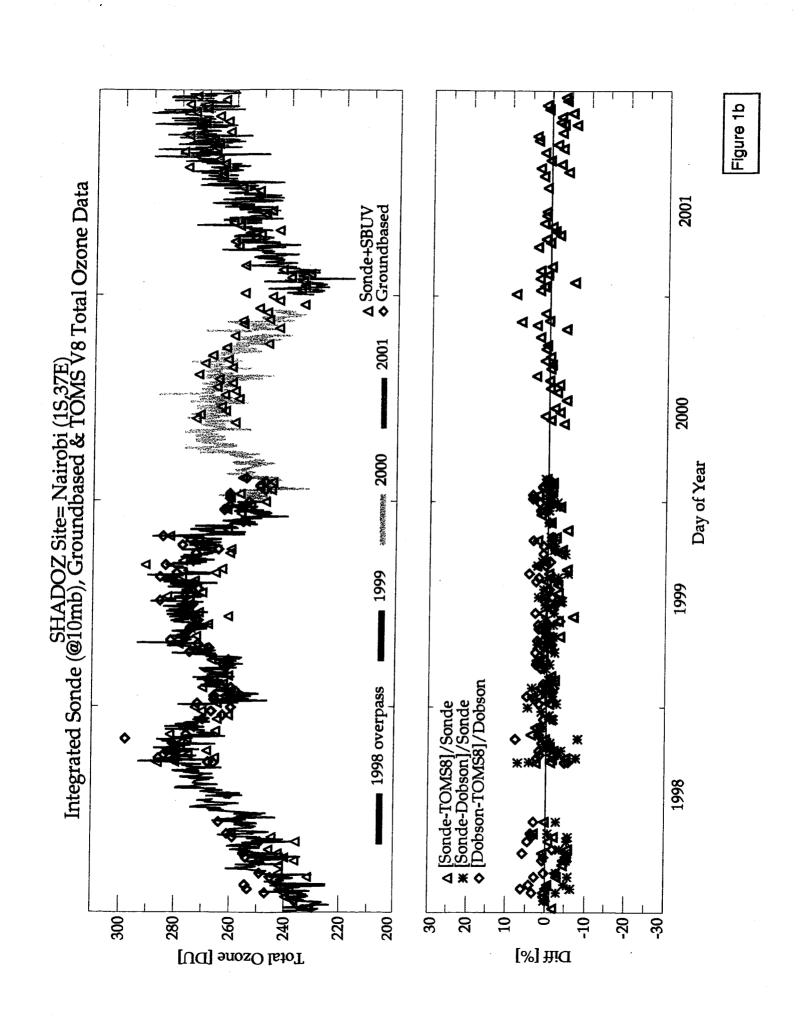
Figure Captions

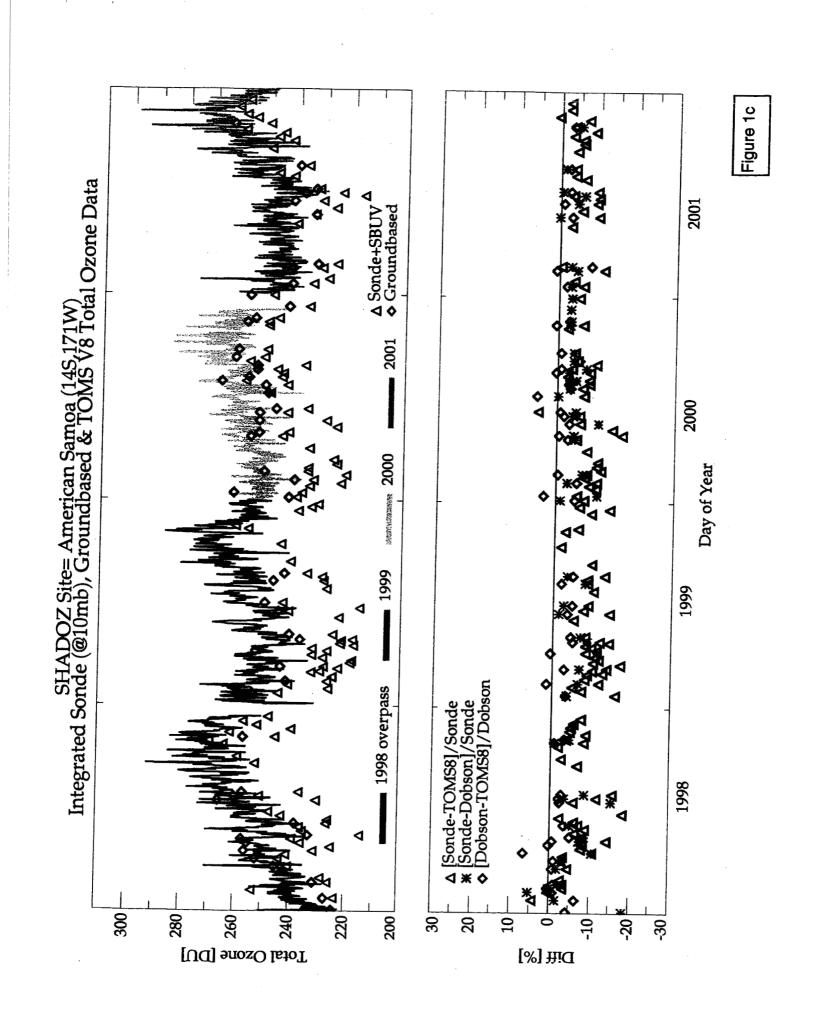
- Fig 1 Upper Panel: A comparison of integrated total ozone from sondes, TOMS satellite (Level 2, version 8) overpasses and Dobson or Brewer instruments at the following SHADOZ stations:

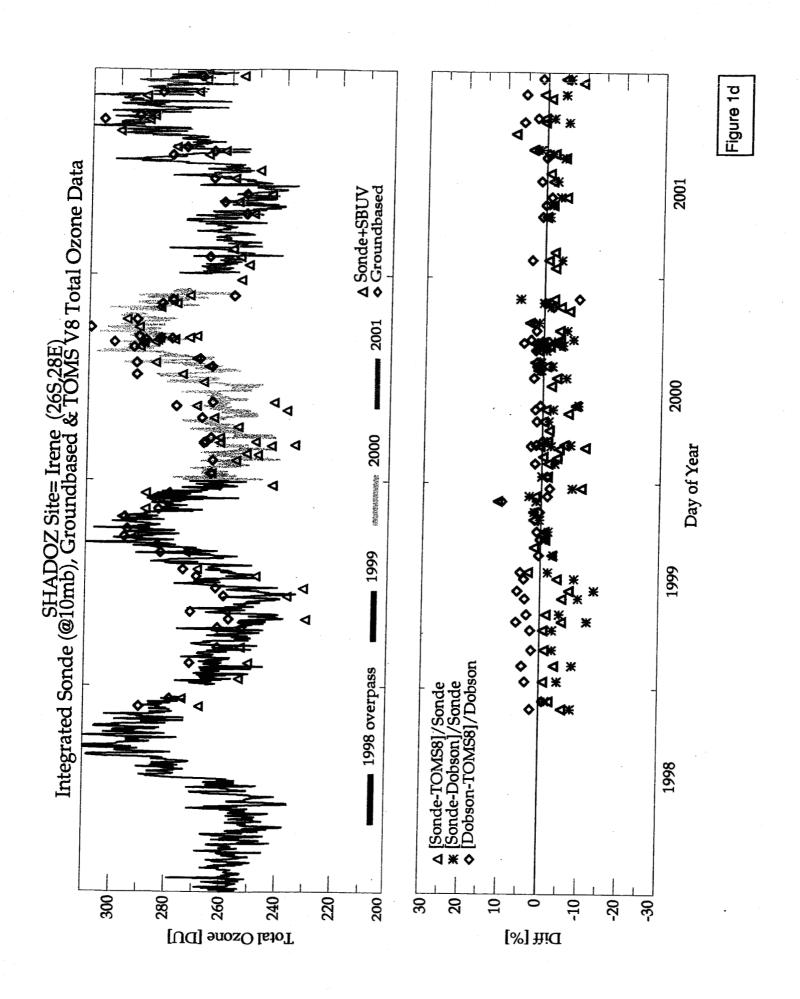
 (a) Natal; (b) Nairobi; (c) Irene; (d) Samoa; (e) Paramaribo. Lower Panel: % deviation relative to the sonde or the ground-based instrument (TOMS version 8). Sonde-ground-based instrument differences are indicated by a *. Integrated ozone from sondes based on data to 10 hPa with extrapolation above 10 hPa from McPeters et al. [1997] climatology. In Thompson et al. [2003a], comparisons are with TOMS v 7 total ozone and sondes reaching 7 hPa before balloon burst. Overall features using v 7 resemble those shown here with v 8.
- Fig 2 Summary of averaged differences between total ozone from SHADOZ sondes and from TOMS (v 7; cf Figure 9, Thompson et al., 2003a) and sondes and TOMS v 8. Data to 10 hPa (Table 3) with SBUV extrapolation are used for sonde total ozone. Shaded region corresponds to "best total ozone" based on Dobsons and most recent TOMS calibration.
- Fig 3 (a) Zonal view of stratospheric column ozone determined from integrated stratospheric ozone of soundings plus SBUV extrapolation. Bars indicate 1-σ standard deviation. For Irene, column may be higher because mid-latitude stratospheric conditions often prevail. The lack of distinct zonal variation in the stratospheric column signifies the absence of a zonal wave-one in the stratosphere. However, uncertainty about the tropopause location introduces 4-5 DU imprecision in the values shown and a wave amplitude smaller than that could not be verified; (b) zonal view of integrated column ozone (DU) between 15 and 20 km, with 1-σ standard deviation; (c) zonal view of the difference between average CMR (constant-mixing-ratio) extrapolations and SBUV for SHADOZ stations.
- Fig 4 Summary of averaged differences between total ozone from SHADOZ sondes and from TOMS (*, v 8, as in Fig 2) with difference between co-located ground-based total ozone and TOMS (□, v 8). Also shown for each station is the mean difference in total ozone between the representative JOSIE-2000 sonde type and the JOSIE-2000 chamber standard (♦, standard = OPM, ozone photometer).
- Fig 5 Mean ozone profiles (from 1998-2002) from soundings that reached 7.0 hPa pressure based on 0.25 km averages. (a) Pacific, eastern Indian Ocean stations: Fiji, American Samoa, San Cristóbal, Watukosek; (b) Atlantic and Kenyan sites: Natal (Brazil), Ascension, Nairobi, Malindi; (c) two sub-tropical stations in SHADOZ, Réunion and Irene. The standard deviation (1-σ) for these averages is +/-1.5 mPa at the stratospheric maximum and ~0.3 mPa elsewhere in the stratosphere. In the middle troposphere, due to large natural variability, the 1-σ standard deviation is ~0.5 mPa at the Pacific stations and > 1 mPa at the others. Constant-

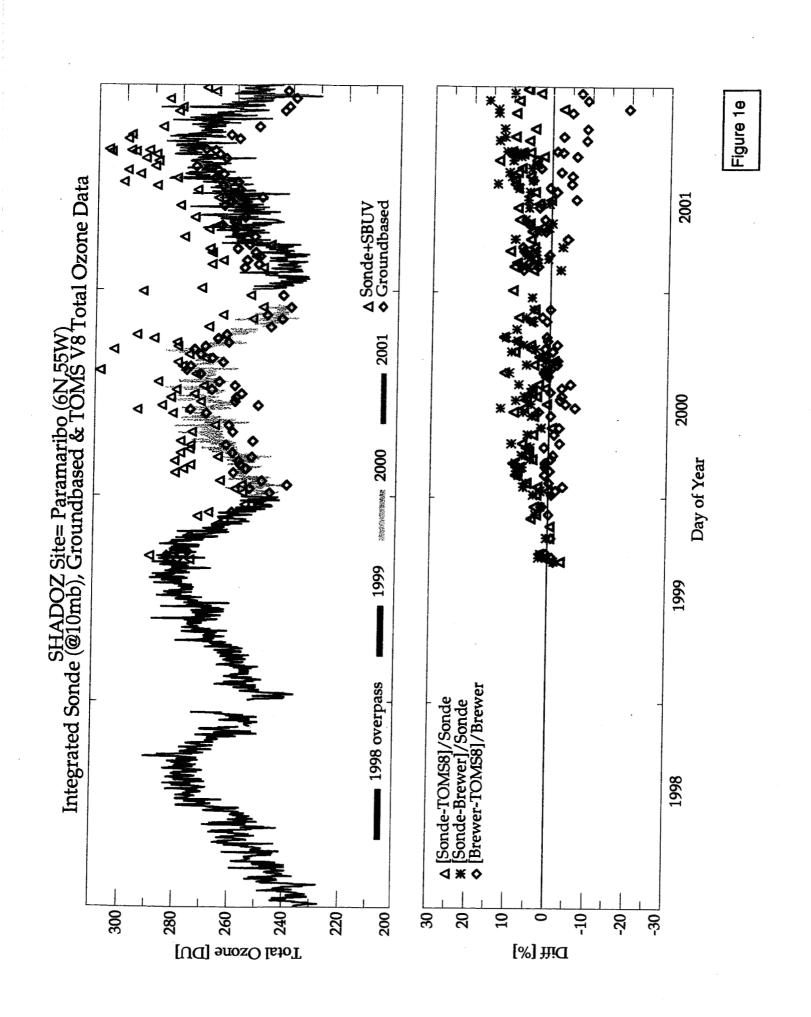
- mixing ratio (CMR) isolines are also illustrated. Our CMR definition uses the uppermost measured points before 7 hPa, then adds a column amount up to 1 hPa. The corresponding mean CMR above 7.0 hPa is given in Table 3.
- Fig 6 Climatological mean profiles based on 1998-2002 SHADOZ data with mean and 1-σ standard deviation (shaded). (a) "tropical" based on all southern hemisphere SHADOZ stations except Réunion and Irene; (b) "sub-tropical" based on Réunion and Irene data. Constant mixing ratio isolines shown.
- Fig 7 Mean SHADOZ station profiles (1998-2002) shown in Figure 5a,b normalized to the climatological mean in Figure 6a. (a) Samoa; (b) San Cristóbal; (c) Fiji; (d) Ascension; (e) Natal; (f) Nairobi; (g) Malindi; (h) Watukosek.
- Fig 8 Same deviations as Figure 7 except stratospheric portion of sonde illustrated from 100-10 hPa. Stations are clustered according to technique used. Also shown are deviations of participant specified corrections (PSC) from OPM standard in JOSIE-2000. (a,b) NOAA/CMDL JOSIE with deviations from SHADOZ tropical mean profile for Samoa, Fiji, San Cristóbal; (c,d) NASA/WFF JOSIE deviations with SHADOZ deviations based on Natal and Ascension data; (e,f) Meteoswiss JOSIE deviations with Nairobi deviation from SHADOZ tropical mean. JOSIE-2000 data are two minute running averages.











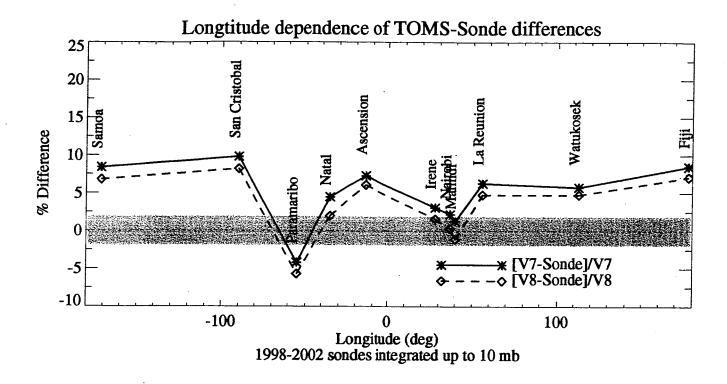


Figure 2

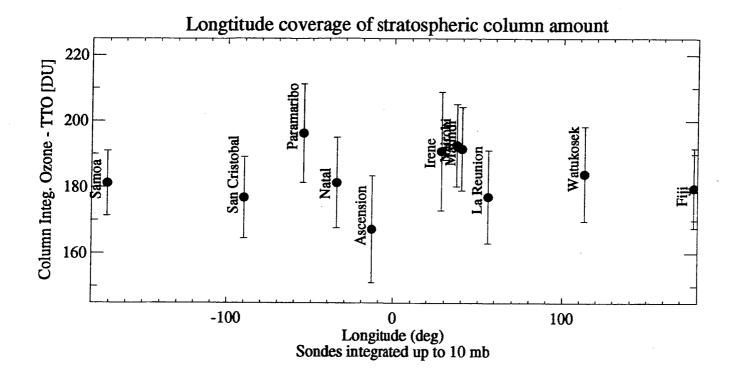


Figure 3a

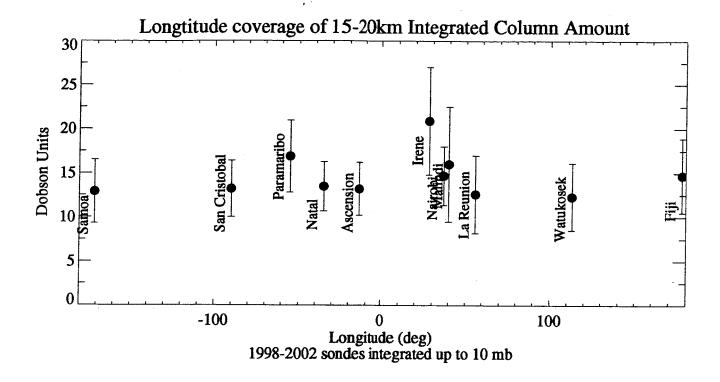


Figure 3b

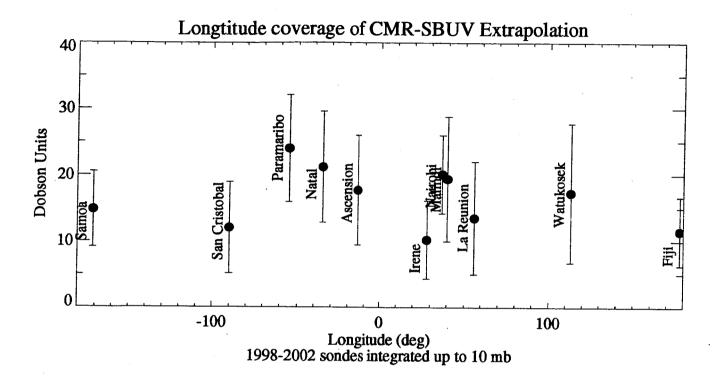


Figure 3c

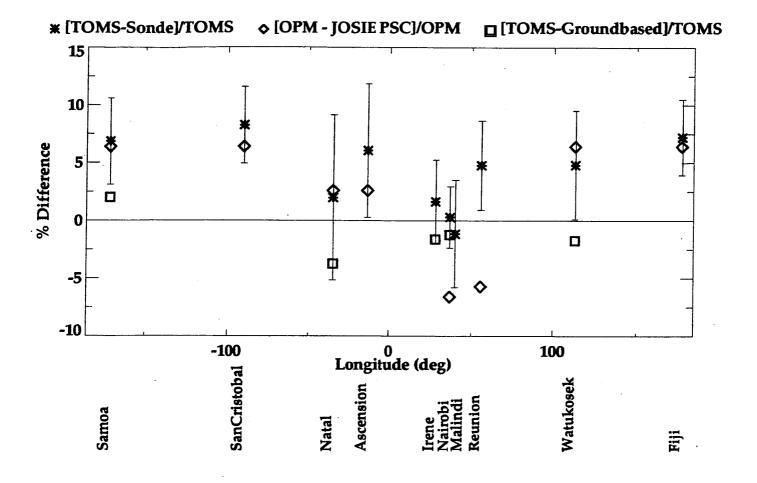


Figure 4

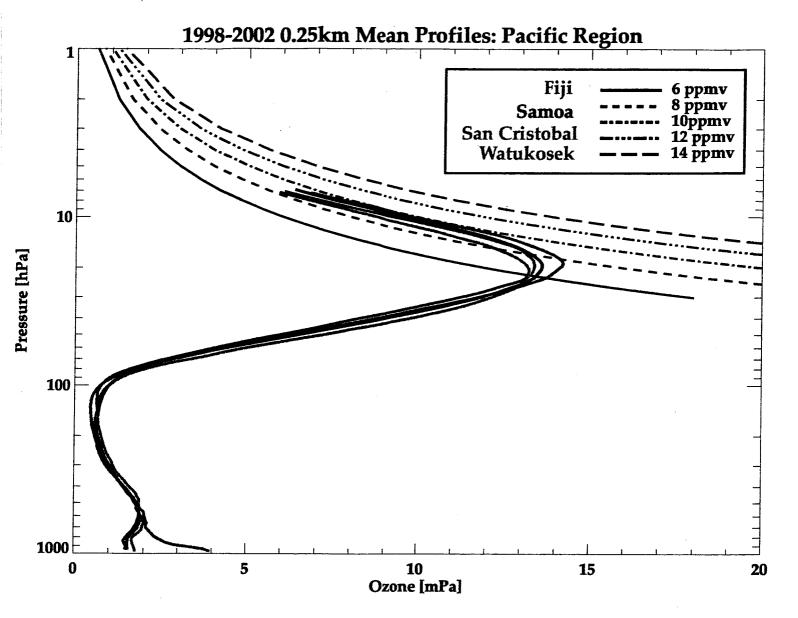


Figure 5a

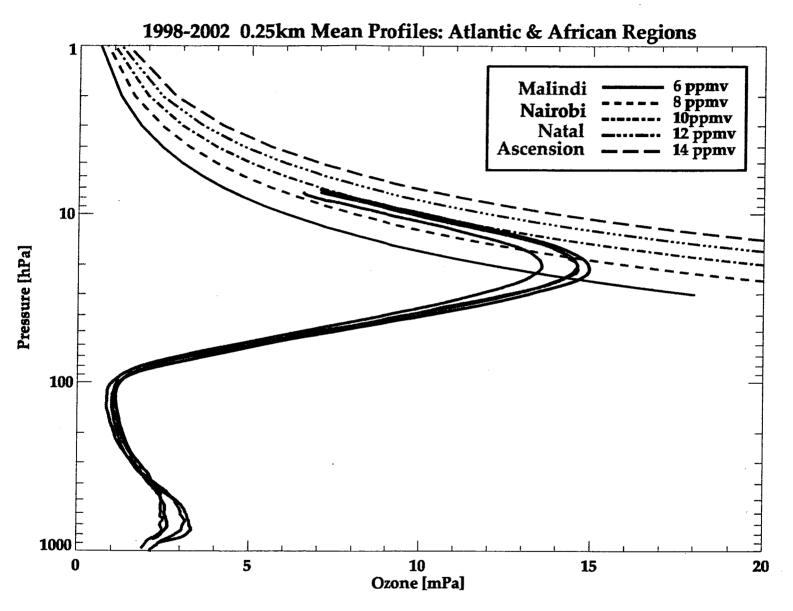


Figure 5b

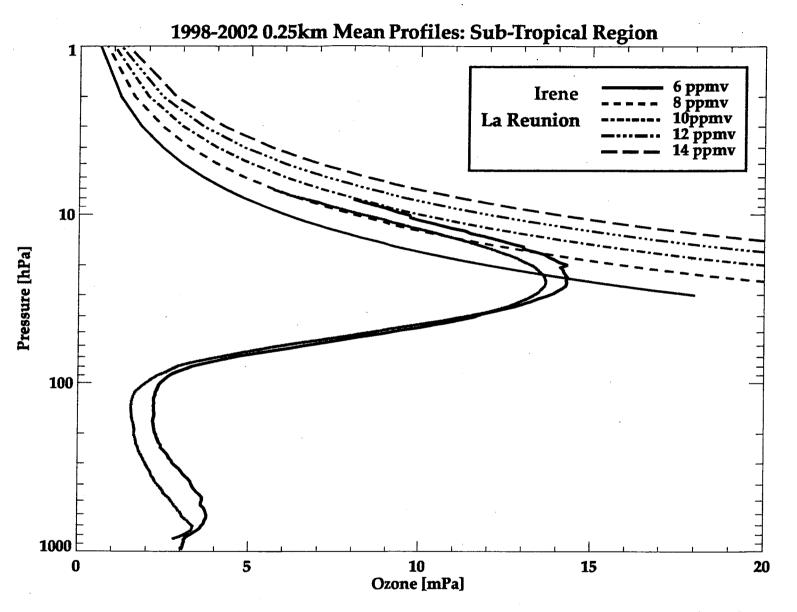
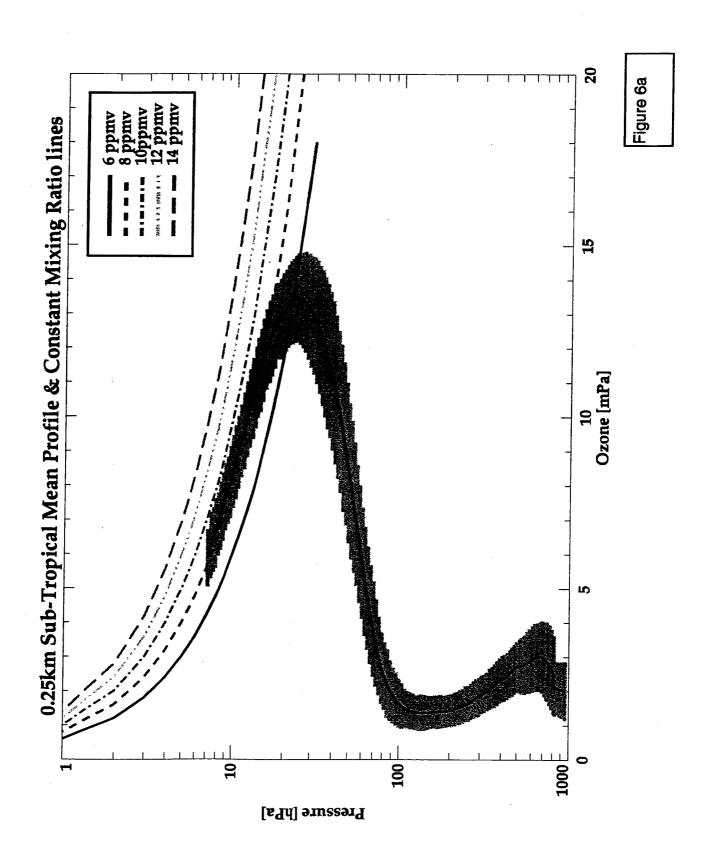
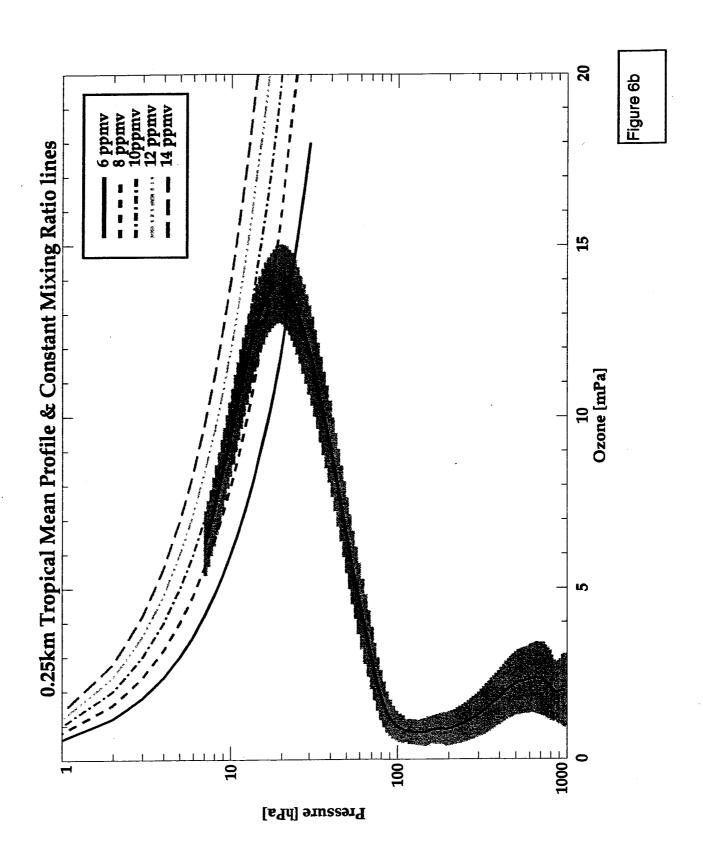


Figure 5c





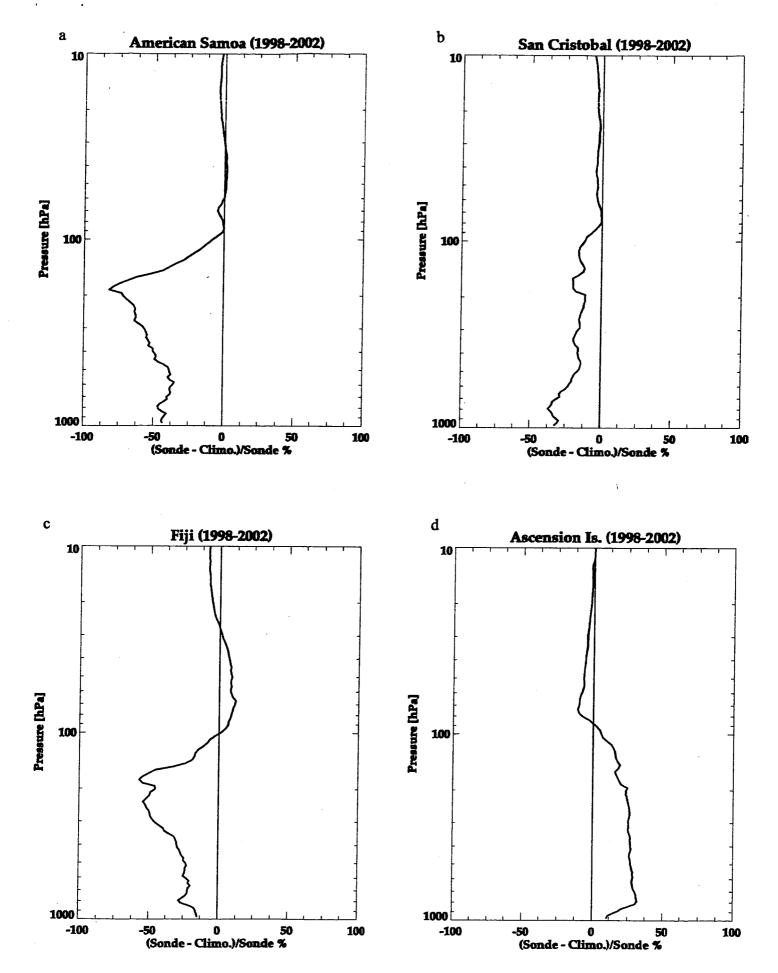
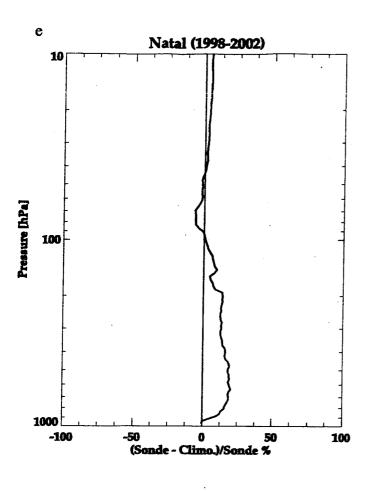
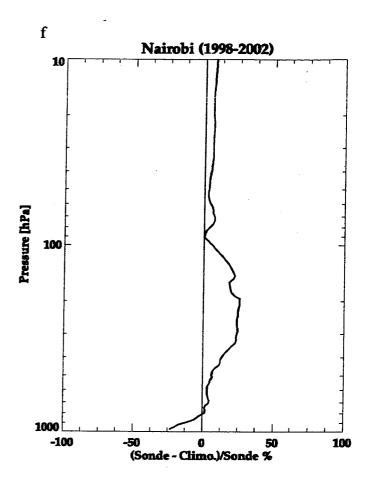
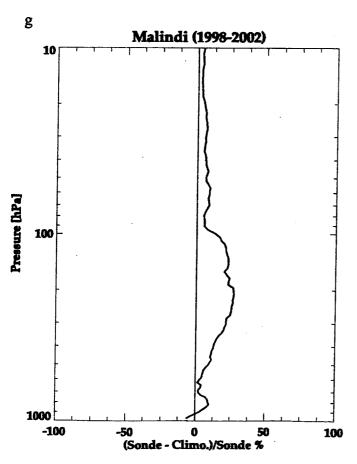


Figure 7







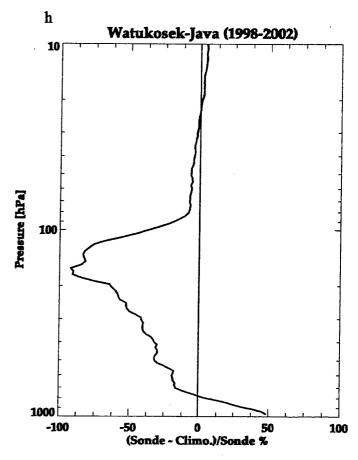
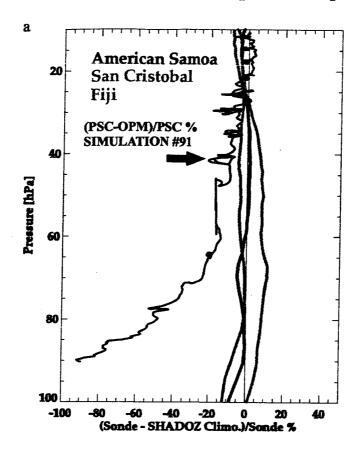


Figure 7 con't

1998-2002 SHADOZ/JOSIE profile comparisons



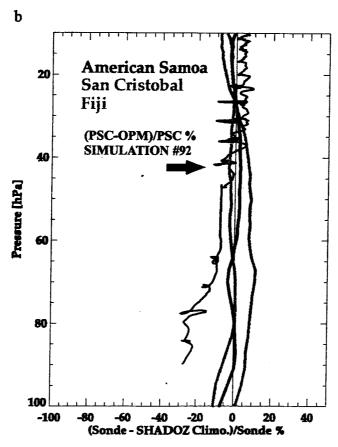
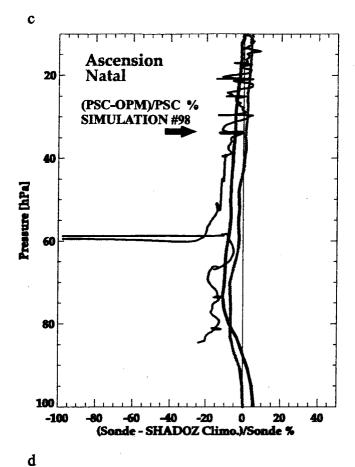


Figure 8



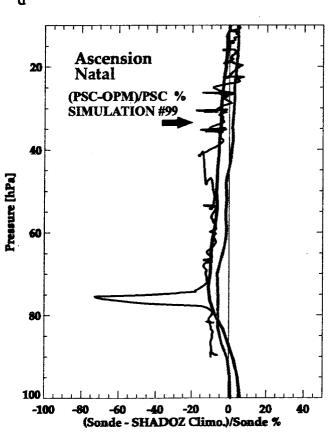


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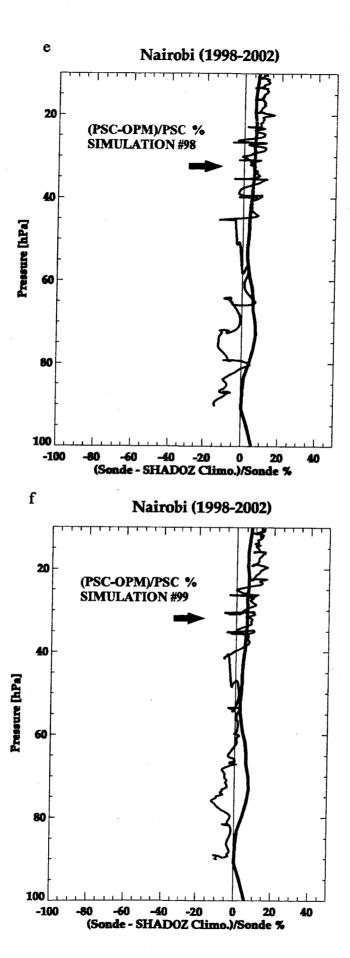


Figure 8 con'd

Popular Summary

The Southern Hemisphere Additional Ozonesondes (SHADOZ) 1998-2002 Tropical Ozone Climatology. 3. Instrumentation and Station-to-station Variability

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Since 1998 the Southern Hemisphere Additional OZonesondes (SHADOZ) project has collected more than 2000 ozone profiles from a dozen tropical and subtropical sites using balloon-borne electrochemical concentration cell (ECC) ozonesondes. See: http://croc.gsfc.nasa.gov/shadoz. It turns out that analysis of ozonesondes data from SHADOZ [Thompson et al., 2003a] revealed that variations in ozonesonde technique might cause station-to-station biases in the ozone readings. In Sept 2000 we had an opportunity to participate in the JOSIE-2000 chamber tests with all the SHADOZ methods mentioned. The purpose was to examine SHADOZ data in the light of the chamber tests. We found that certain variations in SHADOZ ozone profiles are accounted for by differences in solution composition, data processing and instrument (manufacturer). Instrument bias leads to a greater ozone measurement above 25 km over Nairobi and to lower total column ozone at three Pacific sites compared to other SHADOZ stations at 0-20°S. in the measurements. We also in this paper compared SHADOZ total ozone column amounts to version 8 TOMS (2004 release). Discrepancies between sonde and satellite datasets declined 1-2 percentage points on average, compared to version 7 TOMS but were still quite at variance (up to 8%) in total ozone at some sites.

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1 June 2004

The Southern Hemisphere Additional Ozonesondes (SHADOZ) 1998-2002 Tropical Ozone Climatology. 3. Instrumentation and Station-to-station Variability

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Abstract: Since 1998 the Southern Hemisphere ADditional OZonesondes (SHADOZ) project has collected more than 2000 ozone profiles from a dozen tropical and subtropical sites using balloon-borne electrochemical concentration cell (ECC) ozonesondes. The data (with accompanying pressure-temperature-humidity soundings) are archived at: http://croc.gsfc.nasa.gov/shadoz. Analysis of ozonesonde imprecision within the SHADOZ dataset [Thompson et al., 2003a] revealed that variations in ozonesonde technique could lead to station-to-station biases in the measurements. In this paper imprecisions and accuracy in the SHADOZ dataset are examined in light of new data. When SHADOZ total ozone column amounts are compared to version 8 TOMS (2004 release), discrepancies between sonde and satellite datasets decline 1-2 percentage points on average, compared to version 7 TOMS. Variability among stations is evaluated using total ozone normalized to TOMS and results of laboratory tests on ozonesondes (JOSIE-2000, Jülich Ozonesonde Intercomparison Experiment). Ozone deviations from a standard instrument in the JOSIE flight simulation chamber resemble those of SHADOZ station data relative to a SHADOZ-defined climatological reference. Certain systematic variations in SHADOZ ozone profiles are accounted for by differences in solution composition, data processing and instrument (manufacturer). Instrument bias leads to a greater ozone measurement above 25 km over Nairobi and to lower total column ozone at three Pacific sites compared to other SHADOZ stations at 0-20°S.

Index Terms: 0394 - Atmos Structure & Composition - Instruments and techniques; 3309 - Climatology (Meteorology & Dynamics); Regions - 9305, 9325, 9340, 9355/Africa - Atlantic - Indian Ocean - Pacific Ocean; 3394 - Meteorology - Instruments

Free Words - Ozone, Ozonesondes, Satellite Ozone, Tropical Climatology

1. Introduction. Insights from the first three years' SHADOZ ozone data

1.1. Tropical Ozone Profiles: Needs and Status.

In the past 15 years there has been interest in enhancing the number of tropical ozone soundings because important scientific issues are hard to resolve without the vertical resolution provided through these observations. For example, there has been inadequate geographical and temporal coverage in ozone profiles for deducing ozone trends [Logan, 1994; WMO/SPARC, 1998a] in the tropics. Soundings are required to determine the vertical structure of the zonal wave-one pattern in equatorial ozone, detected by Fishman and Larsen [1987] and Shiotani [1992] with satellite data. The wave-one feature refers to more column ozone over the Atlantic and adjacent continents (with a maximum near 0° longitude) than over the Pacific with minimum ozone. Ozone profiles are also needed to evaluate satellite tropospheric ozone estimates (e.g. Fishman and Balok, 1999; Thompson and Hudson, 1999; Ziemke et al., 1998; 2002) and to suggest improved satellite retrievals.

To respond to these and other requirements, the SHADOZ project (Southern Hemisphere Additional Ozonesondes; Thompson et al., 2003a,b) was initiated to augment launches at selected tropical sites and to provide an archive of ozonesonde and radiosonde data at: http://croc.gsfc.nasa.gov/shadoz. Analysis of ~1100 ozone profiles from the 1998-2000 SHADOZ record addressed some of the issues raised above. A longitudinal cross-section of ozone showed that the wave-one is predominantly in the troposphere and occurs throughout the year [Thompson et al., 2003b]. The vertical structure of the stratospheric ozone response to the Quasi-Biennial Oscillation was detailed using balloon data within two degrees of the equator [Logan et al., 2003]. In addition, a SHADOZ campaign of opportunity, the Aerosols99 cruise on the R/V Ronald H. Brown, uncovered an "Atlantic ozone paradox" [Thompson et al., 2000], referring to a higher tropospheric ozone column over the southern hemisphere than over the northern hemisphere during the northern tropical biomass fire season. The paradox, also detected in satellite observations, appears to be a combination of cross-hemispheric transport, photochemical formation of ozone resulting from lightning-derived and pyrogenic precursors and long-range transport of southern Asian pollution interacting with convection [Edwards et al., 2003; Jenkins et al., 2003; Chatfield et al., 2004].

1.2 Ozonesonde Measurement and Impact on SHADOZ.

Besides the above insights into tropical ozone, SHADOZ soundings shed light on ozonesonde technique by providing statistics from an exceptionally large dataset. All SHADOZ stations use ECC sondes (Section 2), but variations in procedures and instrument type (there are two ECC sonde manufacturers) affect the ozone measurement [Komhyr et al., 1995; Johnson et al., 2002; Smit and Sträter, 2004a,b]. Analysis of 1998-2000 SHADOZ soundings [Thompson et al., 2003a] showed the following:

- The precision of the total ozone column by a single instrument is 5%, a value that may be better than previous evaluations [WMO, 1998a,b] because SHADOZ data are taken in a fairly uniform meteorological regime.
- Comparison with ground-based instruments at five SHADOZ stations showed agreement between integrated total ozone from the sondes ranging from 2-7% with the best agreement at Irene (South Africa) and Nairobi.
- Comparison with total ozone from the TOMS satellite (version 7 processing) indicates a fair degree of variability (2-11%) among stations, with the satellite measurement higher, on average, than the sonde total ozone.
- There is no statistically significant difference among the total stratospheric ozone column determined from SHADOZ data between 0-22° S, except for Nairobi, which is ~10 DU higher than the other stations. The Nairobi bias is greatest at the ozone maximum and

- above. Ozone column amounts in the lower stratosphere (15-20 km) are the same at all SHADOZ sites (Figure 12, Thompson et al., 2003a).
- Instrument manufacturer bias, deduced from four SHADOZ stations where a mixture of
 instrument type had been employed, was uncertain. Two stations showed no variation.
 In two others, the ENSCI instrument registered several percent more ozone than the
 Science Pump (SPC) instrument.

Because the World Meteorological Organization (WMO) uses SHADOZ as a model for developing procedures for new stations in the Global Atmospheric Watch (GAW) program, it is important to understand possible instrument influences on the ozone profiles at individual SHADOZ stations. Chamber test experiments (JOSIE series = Jülich Ozonesonde Intercomparison Experiment) were conducted under WMO sponsorship in 1996, 1998 and 2000. In JOSIE-2000, techniques used in the SHADOZ network were intercompared through a standard ozone reference instrument. In this paper:

- Total ozone column amounts from the SHADOZ sondes are compared to version 8 (v 8) TOMS, a new processing of the satellite ozone measurement that uses SHADOZ ozone profiles. Offsets of sonde total ozone with TOMS v 8 and with colocated total ozone instruments from six SHADOZ stations are compared with the corresponding sonde and TOMS version 7 (v 7) offsets.
- Variations in total stratospheric column ozone and upper and lower stratospheric ozone columns are compared among stations to see where biases might occur.
- A SHADOZ climatological "tropical ozone profile" is used to examine variations in ozone profiles at individual sites. The latter results are compared to JOSIE chamber profiles to help interpret ozonesonde performance in SHADOZ operations.

2. Observations and Methods.

2.1 SHADOZ Data.

The SHADOZ ozonesonde measurements are made with electrochemical concentration cell (ECC) ozonesondes, in which air pumped through a cell containing a potassium iodide (KI). Sampled ozone is oxidized producing an electrical proportional to the amount of ozone in the atmosphere [Komhyr, 1967; 1986]. The signals are transmitted to a ground receiver and the ozone partial pressure is recorded through comparison with the pressure readings of an accompanying radiosonde. Designed to measure ozone concentrations from the surface to above the ozone concentration maximum, the ozonesonde-radiosonde package is flown with a balloon that usually bursts at 4-8 hPa.

SHADOZ was initiated (January 1998) with nine southern hemisphere stations and presently numbers twelve sites. Irene soundings began in late 1998 and Paramaribo, the first northern hemisphere station, started in late 1999. Launches are nominally weekly, with occasional additions during field campaigns. Experimental details are at: http://croc.gsfc.nasa.gov/shadoz and in the Appendix of Thompson et al. [2003a]. A summary of station technique, latitude and longitude appears in Table 1.

For the present analysis, sounding data from the SHADOZ archive for 1998-2002 are used except in comparisons with TOMS where 1998-2001 data are employed. After 2001 the Earth-Probe (EP)/TOMS instrument diverged too much from the Dobson network to be reliable for our purposes [R. McPeters, personal communication, 2004].

The sonde instrument is not ideal for calculating total ozone because typically 15-20% of the ozone column is above the balloon burst, the pressure measurement of the radiosonde can become become noisy and the sampling pump rate changes. Note the following about our calculations of total ozone from SHADOZ sondes. First, no normalization is made to total ozone from another instrument, such as a satellite or a co-located ground-based total ozone sensor.

Second, only data from balloons that reached at least 10 hPa are used in computing integrated ozone. During the 1998-2000 period 75% of SHADOZ launches reached 7 hPa (analyzed in Thompson et al., 2003a). For the present analysis we choose a larger set of profiles with the 10 hPa criterion. To integrate to 1 hPa, an "evaluated ozone residual" from the SBUV satellite climatology of McPeters et al. [1997] gives an extrapolation from 10 hPa or balloon burst, whichever is higher. Extrapolation by assuming a constant mixing ratio (CMR) for ozone above balloon burst is useful for some diagnostic purposes but gives an erroneous total ozone. The third feature of SHADOZ records is that a TOMS overpass value is taken from the orbit that passes most closely to the station at roughly local noon. Most stations launch ozonesondes between 0700 and 1000 local time, so the satellite and sonde measurements are well-matched.

2.2 The Ozonesonde Measurement. JOSIE-2000.

Differences in data processing, as well as in sonde manufacturer and instrument preparation, can contribute to systematic variations among ozone measurements. Johnson et al. [2002], Thompson et al. [2003a] and Smit and Sträter [2004a,b] describe factors that may affect the ozonesonde measurement at SHADOZ sites. These include (a) the background current; (b) the concentration of potassium iodide (KI) in the cell anode and cathode; (c) strength of any buffer used; (d) the factor used to correct for the decline in pump efficiency as the sonde ascends. JOSIE experiments conducted in 1996, 1998 and 2000 suggested that these factors could be significant [WMO, 1998b; Smit and Sträter, 2004a,b], although (a) has become a more minor issue with improvements in cell manufacture. SHADOZ stations include a range of solution composition (Appendix in Thompson et al., 2003a) and at least two methods of applying the factor to correct for pump efficiency (PCF). For example, the technique at the four Pacific stations in SHADOZ is uniform and the same instrument type (SPC) is normally used. Likewise, uniform procedures are employed at Natal and Ascension (differing sensor concentration from the Pacific stations), normally with the SPC instrument.

The instrument type and sensing solution were varied in the JOSIE-2000 campaign, as shown in Tables 1 and 2. Two teams of four investigator groups participated. Each group prepared instruments for eight chamber simulations. The tests were conducted at the Forschungzentrum-Jülich environmental simulation facility [Smit et al., 2000; http://www.fz-juelich.de/icg/icg-ii/esf, established as a World Calibration Centre for Ozonesondes (WCCOS) to aid in quality assurance within the WMO/GAW network. Two tropical, two sub-tropical and two mid-latitude simulations were carried out by each group along with response time tests. Data displayed here were processed by Smit and Sträter [2004a,b]. Further details of JOSIE operations appear at the website: http://www.fz-juelich.de/icg/icg-ii/josie.

Table 2. JOSIE-2000 tests simulating SHADOZ conditions.

Test Date	Simul. No.	Condition	SHADOZ Participant
10 Sept 2000	91	Tropical	NOAA/CMDL
11 Sept 2000	92	Tropical	ш
14 Sept 2000	94	Sub-tropical	ш
15 Sept 2000	95	Sub-tropical	"
20 Sept 2000	98	Tropical	NASA/WFF, Meteoswiss, Univ. Réunion
21 Sept 2000	99	Tropical	ш

24 Sept 2000	100	Sub-tropical	"
26 Sept 2000	102	Sub-tropical	"

3. Total Ozone: Comparison to Independent Measurements, Station Variability

Accuracy of the sonde total ozone measurement from 1998-2000 data was evaluated through comparison with total ozone measured by co-located ground-based instruments (Dobson and Brewer) at five SHADOZ sites (Figures 6 and 9 in Thompson et al, [2003a]). At each station, total ozone is also compared to the EPA/TOMS overpass total ozone column.

3.1 Total Ozone Comparisons - TOMS version 8

Figure 1 shows daily TOMS overpass data (v 8 processing, 2004 release) for 1998 through 2001 for five stations, together with total ozone integrated from the sonde (as described in Section 2) and ground-based instrument (α and \bullet symbols, respectively). The ground-based Dobson spectrophotometers are regularly calibrated (four sites). At Paramaribo the ozone column is based on a Brewer instrument [Peters et al., 2004]. In the lower panel, offsets among sonde, TOMS, and the ground-based instrument are shown. Total ozone comparisons similar to those in Figure 1 were depicted in Thompson et al. [2003a] using TOMS v 7 ozone.

The ozone column measurement from the sondes in Figure 1a is >5% lower in 1998-1999 compared to 2000 onward. From 1997-1999 a change in the solution composition recommended by the ENSCI manufacturer (0.5% KI compared to 1%) was employed at Natal even when the SPC sonde was flown. This is consistent with results of the JOSIE tests. During JOSIE-2000 it was shown that when the same instrument type and data processing are used, the 0.5% KI solution gives an averaged 5% lower ozone throughout the profile than does the 1% KI solution [Smit and Sträter, 2004b]. In addition to known changes in the sonde technique at Natal, there is evidence in both the colocated Dobson and Brewer instruments (the latter not shown) that TOMS ozone declined and became more variable in 2001 compared to the prior four years. Similar behavior among Brewer, Dobson and TOMS ozone was noted at Cachoeira Paulista, Brazil (23S, 38W; V. W. J. H. Kirchhoff and N. Paes Leme, unpublished manuscript, 2004).

The African stations are those with the closest agreement between TOMS and the sonde total ozone column (Figures 1b,c). This holds throughout the SHADOZ record, although the Dobson at Irene seems noisier in 1998 than later on. Both the Nairobi and Irene Dobson instruments were calibrated with the traveling world standard Dobson in Pretoria in April 2000. Data from the Nairobi Dobson are not available after that time. Judging from the sonde and Dobson, the TOMS instrument appears stable over Irene from 1998-2001. In Thompson et al. [2003a] it was noted that Irene and Nairobi are the two SHADOZ stations with elevation > 1 km. This possibly implied better agreement at sites with less tropospheric air mass because TOMS is not very sensitive below 500 hPa [Hudson et al., 1995]. However, Thompson et al. [2003a] also found (cf Figure 3 below) that much of the disagreement between TOMS total ozone and the sonde integral originates in the stratospheric part of the ozone profile. With Figure 2 showing similar TOMS-sonde offsets at Malindi (sea-level) and Nairobi (1.3 km altitude, 400 km from Malindi), there is further evidence that tropospheric discrepancies do not dominate.

At Samoa (Figure 1d) TOMS total ozone appears to be declining relative to the sonde measurement, although the early 1998 sonde data are too noisy to be definitive in this respect. There is less drift in TOMS compared to the Dobson. The tendency for the TOMS ozone column to exceed that of the Dobson by overestimating tropospheric ozone in the satellite algorithm (Figure 8c in Thompson et al., 2003b), appears unchanged in the transition from v 7 to v 8.

At Paramaribo (Figure 1e) sonde total ozone is consistently greater than the TOMS v 8

measurement and the Brewer is frequently less than the satellite ozone. In both cases, though less than three years of data are given, a TOMS downward drift is suggested in the second half of 2001. Sonde total ozone is nearly 10% higher than TOMS, on average, at that time. Paramaribo is north of the ITCZ most of the year, quite distinct from other SHADOZ stations and the ozone profile (and integrated column) may indeed diverge from them. Accordingly, in most subsequent comparisons, we do not compare Paramaribo data with the southern hemisphere data.

In Figure 2, where the TOMS-sonde total ozone differences are displayed for both v 7 and v 8 TOMS, Paramaribo shows a negative deviation. Figure 2 also shows a tendency for the Pacific SHADOZ stations and Watukosek to be biased lower relative to TOMS than the Atlantic and African stations. One reason for this is that the TOMS algorithm (both versions 7 and 8) assumes a greater tropospheric ozone column depth (29.8 DU; Table 4 in Thompson et al., 2003b) than actually measured at the Pacific stations (mean tropospheric column depth, ~19 DU). There is only a 1-2 percentage point change to the TOMS-normalized data at the SHADOZ stations (Table 3) using v 8 compared to v 7. However, agreement between the southern hemisphere Dobson stations and TOMS v 8, spanned within the shading in Figure 2, improved over v 7 (compare offsets shown in [Bodeker et al., 2001]).

3.2 Stratospheric Ozone Comparisons from SHADOZ Sondes

We also examined the integrated stratospheric ozone column to see whether some of the SHADOZ station variability is due to stratospheric ozone variability among the sites (refer to Figures 10-12 in Thompson et al. [2003a]). These analyses are performed with the 1998-2002 sondes in three ways, as illustrated in Figures 3a-c. The total integrated stratospheric ozone column in Figure 3a includes the measured ozone column to 10 hPa and the SBUV extrapolation. The latter quantity is an average by month and latitude band, i.e., 0-10N, 0-10S, 10-20S [McPeters et al., 1997]. The range of SBUV extrapolation values used for 10-1 hPa is 36-48 DU. Figure 3a, which presents the total integrated stratospheric ozone column (± 1-σ), shows all the stations overlapping except for Ascension Island (lowest at 167 DU) and Paramaribo (highest at 196 DU). All other SHADOZ stations are within the range 177-192 DU. In Thompson et al. [2003a] it was concluded that the SHADOZ record does not show a statistically significant stratospheric wave-one pattern. Additional data in the present analysis (~40% more profiles than in Thompson et al. [2003a]) lead to the same conclusion.

Two diagnostics are used to look more closely at stratospheric variability: the 15-20 km integral (~110-60 hPa) and the CMR extrapolation. Figure 3b, depicting the lower stratospheric integrated ozone column, shows almost no variation among the SHADOZ stations (compare Figure 11 in Thompson et al. [2003a], where 1998-2000 data were used). An exception is Irene, where roughly half the observations are made at mid-latitude conditions. Not counting Irene, the range of mean 15-20 km ozone column is ~4 DU. The 15-20 km ozone column uniformity is taken as further evidence for the lack of a stratospheric wave because zonal variation is expected in the lower stratosphere [Shiotani and Hasebe, 1994; Newchurch et al., 2001].

The CMR is used to diagnose the relative behavior of the upper stratosphere which is not expected to vary among the southern hemisphere SHADOZ sites. In Figure 3c, raw CMR values are not displayed but rather their deviation from the SBUV add-on for each station (Table 2). Variations in the CMR-SBUV parameter may reflect the effect of the sensing solution, the instrument used or data processing (primarily the PCF employed by each station Co-Investigator). Here, in contrast to the lower stratosphere bias (Figure 3b), the range across the SHADOZ stations exceeds 10 DU. The Atlantic stations (Paramaribo-Natal-Ascension) are relatively high whereas for total stratospheric ozone, Natal and Ascension are relatively low (Figure 3a). Irene, Fiji and San Cristobal are the lowest in normalized CMR. Can the precision

of the stratospheric quantities be estimated using the CMR normalized statistics? The Natal-Ascension pair and Fiji-Samoa pair are only 4 DU apart. Nairobi and Malindi, stations ~400 km apart, are within 2 DU of one another in all three stratospheric analyses shown in Figure 3.

3.3 Implications of JOSIE-2000 for SHADOZ Total and Stratospheric Ozone

How do we interpret some of the apparent systematic differences among SHADOZ stations? The possibility of instrument effects is considered by referring to selected JOSE-2000 results. First, the deviation between integrated ozone from the sonde in the chamber relative to the ozone photometric (OPM) standard is compared to normalized total ozone from SHADOZ sites. In other words, TOMS, the ground-based instruments and the OPM are treated as standards through which the sonde ozone total is intercompared. Figure 4 depicts the following:

- Ozone data from the test chamber integrated from surface conditions to 10 hPa using the
 appropriate instrument type for a given SHADOZ station differenced with the integrated
 ozone from the JOSIE-2000 OPM. The chamber ozone column was computed with the
 participant's own pump correction factor to capture possible processing biases as well as
 effects of instrument type and sensing solution.
- Ozone integrated from the SHADOZ station sondes relative to TOMS total ozone from satellite overpasses (as in Figure 2).
- Total column ozone from ground-based instruments at five SHADOZ stations (four Dobsons, one Brewer) differenced to the TOMS overpass total ozone.

Figure 4 shows that differences between sonde total ozone from the three Pacific stations and Watukosek and v 8 TOMS (with the sonde reading low relative to the satellite) are mostly consistent with the JOSIE-2000 results. The field instruments (SPC) read ~7% lower than TOMS at Samoa and Fiji. That is nearly identical to the JOSIE deviation from the OPM and within 2% of the TOMS-sonde offsets at Watukosek, where the same technique (NOAA/CMDL method) is used. The TOMS-sonde agreement at San Cristóbal is similar to Samoa and Watukosek but the TOMS-sonde discrepancy is slightly worse than the JOSIE sonde-OPM disagreement. Dobson-TOMS (Samoa) and Brewer-TOMS (Watukosek) offsets are smaller (2% absolute) than the sonde-TOMS offsets for these stations and for San Cristóbal and Fiji.

Natal shows close agreement between the sonde-TOMS discrepancy (Figure 4) and the JOSIE-2000 chamber tests, where the sonde ozone total was ~2.5% lower than the standard. The Dobson, however, was ~2.5% higher than TOMS ozone at Natal. Also, in Figure 4, JOSIE-2000 tests show the instrument type (ENSCI) reading greater in total ozone than the OPM standard for the Réunion and Meteoswiss (Nairobi) participants. The sondes recorded 6-7% greater ozone than the reference. For the corresponding SHADOZ measurements at Nairobi, total ozone normalized to TOMS reads higher than at all other stations but one (Malinidi). However, the TOMS-sonde offset at Nairobi is less than the bias of the corresponding JOSIE instruments. The TOMS-sonde offset based on Réunion measurements differs nearly 10% from the chamber tests.

4. SHADOZ Ozone Profile Analysis

Although there are relatively small differences in stratospheric ozone column among SHADOZ stations, it is important to evaluate variability arising from the ozone measurement in various parts of the profile. This is done in two steps. First, mean SHADOZ ozone profiles from each station are compared to an overall mean SHADOZ profile. Second, biases in the stratospheric ozone segments at SHADOZ stations are compared to corresponding behavior of the station technique as tested in JOSIE-2000.

4.1 Characteristics of Mean SHADOZ Profiles

Figure 5 shows the mean profile from each southern hemisphere SHADOZ station. The CMR isolines are drawn to show tendencies for upper stratospheric variability among the SHADOZ stations. What is observed? For the three Pacific stations and Watukosek (Figure 5a).

ozone profiles are nearly identical in the lower stratosphere but there is divergence at the stratospheric maximum. For Watukosek the maximum occurs at ~15 hPa and the corresponding partial pressure is 14 mPa. For Fiji the maximum partial pressure is ~13mPa. Extrapolations above 7 hPa (the minimum pressure plotted) fall between the 8 and 10 ppmv isolines. The tropospheric profiles of the three Pacific stations are similar in integrated column amount and shape. At the surface, ozone is < 2 mPa (14.5 ppbv), declining to the top of the mixed layer. Ozone then increases to ~600 hPa where a second decline begins that continues to the tropopause. The lower tropospheric layer of maximum ozone is due to imported pollution. Only at Watukosek, among SHADOZ sites, does pollution-level ozone occur at the surface.

Figure 5b shows that the two Atlantic and two Kenyan stations are similar in the stratosphere (~ 15 mPa at maximum) except for Ascension where the maximum partial pressure is < 14hPa. The upper stratosphere ozone (signified by CMR isoline at 12 ppmv) for Natal, Nairobi and Malindi is also greater than for Ascension. In the troposphere, Natal and Ascension have peak ozone partial pressure at 700 hPa, a consequence of long-range transport of pollution. Back-trajectories initialized at 700 hPa from Natal and Ascension on days of ozonesonde launch (images available at the SHADOZ website) show African origins for the highest ozone episodes. The two sub-tropical SHADOZ stations (Figure 5c) have peak ozone partial pressure closer to 30 hPa than to 20 hPa (compare the tropical maximum in Figures 5a,b). Sub-tropical profiles are signified by more ozone throughout the lower stratosphere and upper troposphere. In the uppermost stratosphere, Irene and Réunion differ, with the latter always higher. This causes a 5 DU difference in the normalized CMR between the two stations (Figure 3c).

For purposes of examining relative features of individual station profiles, it is useful to define "mean tropical" and "mean sub-tropical" ozone profiles from SHADOZ data. These can be viewed as analogous to the JOSIE-2000 OPM "standard" tropical and sub-tropical profiles. A SHADOZ "mean tropical" ozone profile, with 1-σ standard deviation (Figure 6a), is based on the eight stations illustrated in Figures 5a and 5b plus 1998-1999 statistics from Tahiti (see Table 3 in Thompson et al. [2003a]). For Watukosek, only data from after July 1999, when soundings with ECC instruments were initiated, appear in the average. Likewise, the Réunion (21°S) and Irene (26°S) ozone data are used to define a SHADOZ "mean sub-tropical" ozone profile (Figure 6b.) The integrated ozone column amounts show a tropical-sub-tropical difference of ~15 DU: Integrated ozone, surface--10 hPa: 189.4 DU, tropical 206.1 DU, sub-tropical Integrated ozone, surface--7 hPa: 212.5 DU, tropical 225.4 DU, sub-tropical

SHADOZ Ozone Profile Climatologies Relative to Means 4.2

In Figure 7a-h individual station ozone profiles, normalized to the SHADOZ tropical mean, are depicted. Positive deviations signify a higher bias at the same pressure at a SHADOZ station relative to the climatological ozone value. Tropospheric absolute deviations sometimes exceed 40%. In the stratosphere (taken as above 100 hPa for convenience), the deviations rarely exceed 10%. On average, above 70 hPa, Samoa (Figure 7a) is closest to the climatological mean with absolute deviation < 5% up to 10 hPa. Above 80 hPa San Cristóbal (Figure 7b) is also close to the climatology and the shape is quite uniform throughout the stratosphere. Fiji is distinctive among the stations illustrated (Figure 7c) in having the largest positive deviation in the lower stratosphere between 40 and 95 hPa. Ascension and Natal (Figures 7d,e) parallel one another in the stratosphere. There is a monotonic change in the deviation, starting from station sondes biased low relative to climatology. At 10 hPa, both are within 5% of the mean ozone value and 5-10% greater than Samoa, San Cristobal and Fiji at 10 hPa. Nairobi deviations (Figure 7f) resemble Ascension and Natal throughout most of the stratosphere. An exception is in the 80-60 hPa range where the Nairobi sondes are greater than climatology by ~5% and Ascension and Natal (Figures 7 d,e) are low by 5-10%. Malindi (Figure 7g) has positive deviations throughout

the stratosphere, similar to Nairobi (Figure 7f). Watukosek (Figure 7h) has the greatest deviation from the mean at the 100 hPa level but above 60 hPa is always within 5% of the mean.

The results shown in Figure 7 are explored further to see if the tendencies recorded in ozone above 100 hPa are consistent with the total ozone patterns and with independent evaluation of the SHADOZ technique. First we ask: (1) How do the profile deviations from a SHADOZ tropical climatology (depicted in Figure 7) compare to variability in total ozone from among the stations? The information summarized in Figure 7 is compared to Figure 3 and Table 3. Figure 3 showed that column-integrated stratospheric ozone to 10 hPa at Samoa, San Cristóbal, Watukosek and Fiji fall within a 7 DU (177-184 DU) range of one another. This is consistent with Samoa and San Cristóbal having profiles close to the tropical mean (Figures 7a,b). The deviations within the Fiji profile (Figure 7c), positive above 30 hPa and negative below, apparently cancel out in the stratospheric integral. Table 3 (also Figure 3a) shows the Fiji stratospheric column (179.7 DU) close to the all-southern tropical station mean (181.8 DU).

Figure 3 and Table 3 show Ascension ~10 DU less in stratospheric column than the other stations whereas Nairobi and Malindi are ~10 DU greater. Figure 7 indicates how these variations might come about. The Ascension stratospheric profile (Figure 7d) is 5% lower than climatology, on average, throughout the stratosphere. However, at 80-100 hPa, Ascension is greater than climatology so the 15-20 km column integral (Figure 3b) does not deviate significantly from the other stations. Natal (Figure 7e), like Fiji, has deviations both positive and negative so that its stratospheric integral falls near the mean (Figure 3a). Nairobi and Malindi (Figures 7f,g) are roughly 5% higher than the climatological profile throughout the stratosphere.

4.3 SHADOZ Profile Biases and JOSIE-2000 Results

How do the deviations at individual SHADOZ stations, relative to the tropical climatology, compare to profile deviations for the given technique as recorded in the JOSIE-2000 tests with a reference ozone standard? Figure 8 illustrates the stratospheric offsets from the SHADOZ climatology (as in Figure 7) along with deviations between the corresponding chamber instrument and the JOSIE OPM. The latter deviations plotted are based on the participants specified corrections (PSC). Figure 7 in Johnson et al. [2002] shows that the PSC adds 5-10% to the measured value above 100 hPa for all but one method used in SHADOZ (Table 1; see also Table A-1 in Thompson et al. [2003a]). The exception is a higher PSC (up to 20% added) used where the NOAA/CMDL technique is employed (four Pacific stations and Watukosek after July 1999).

Comparisons are given for three instrument types: NOAA/CMDL method (Samoa, Fiji, San Cristóbal, Figures 8 a,b); NASA/WFF method with Natal and Ascension (Figures 8 c,d); the Meteoswiss method with Nairobi (Figures 8e,f). Figures 8a and 8b represent two tropical JOSIE-2000 simulations and display, respectively, the deviations of the sonde from the OPM standard with the NOAA/CMDL sensing solution (2% KI, no buffer) in cells of SPC and ENSCI manufacture. The NOAA/CMDL method is low (~50%) compared to the OPM at 100 hPa. As the pressure falls below 60 hPa, agreement improves to within 10% of the standard, averaging a little below the OPM in Figure 8a (the SPC instrument) and a little above the OPM (ENSCI) in Figure 8b. For the NASA/WFF (Figure 8c,d) and Meteoswiss (Figure 8e,f) methods, JOSIE-2000 also shows an underestimate of ozone relative to the OPM in the 100-60 hPa range, though of less magnitude (10-20% deviation) than the NOAA/CMDL method. Deviations of NASA/WFF JOSIE and SHADOZ Natal sondes minimize at 40 hPa (Figure 8c,d).

In Figure 8 the low-ozone bias in all cases in the 100-60 hPa region in the JOSIE-2000 tests reflects the very low absolute ozone amount at 100 hPa in the simulated profile. The sonde responses, determined in pre-experiment tests (or pre-launch, in the field), are typically 22-35 seconds, whereas the photometer senses an ozone change within a second. In the chamber

simulation, the ozone partial pressure was nearly zero from 180-100 hPa. Above 100 hPa, as in the tropical atmosphere, ozone increases sharply but the sondes never respond as quickly as the photometer. As ozone continues to increase with decreasing pressure, the percentage lag is less; the agreement with the OPM improves.

Differences among sonde performance in the JOSIE-2000 stratospheric simulations also reflect variations in the sonde sensing solution and ECC instrument type. The large contrast in sonde response in the 100-60 hPa range when the NOAA/CMDL method (Figure 8a,b) is compared to the other two methods (Figures 8c-f) stems from a difference in buffering of the KI solution. After a strong ozone signal has been measured, a buffered solution responds to lower ozone sluggishly, a "memory" effect. The unbuffered NOAA/CMDL solution (Figure 8 a,b) appears to have a greater lag in the 100-60 hPa region relative to the NASA/WFF and Meteoswiss instruments (with buffered solutions) because there is no memory from previous measurements. Thus, the apparent better ozone response of the NASA/WFF and Meteoswiss instruments in the lower stratosphere, either simulated or when Fiji offsets (Figure 8a,b) are compared to Natal or Nairobi (Figures 8c-f), for example, is partly an artifact of the solution.

The impact of buffering may be significant in the upper stratospheric portion of the ozone profile (40-10 hPa in Figure 8) where the ozone maximum occurs. However, this influence is more difficult to gauge because PSCs are included in both the JOSIE-2000 and SHADOZ data. In the case of the NOAA/CMDL method (Figure 8a,b) the JOSIE-2000 tests show a slight positive bias above 20 hPa but the SHADOZ data are all relatively low compared to the tropical climatology. Fiji, Samoa, San Cristóbal ozone deviations (Figure 8a,b) average ~15% lower than ozone at Nairobi above 20 hPa (Figure 8e,f) and 5-10% lower than Natal (Figure c,d).

The Meteoswiss JOSIE-2000 results and SHADOZ Nairobi sonde deviations (Figure 8e,f) generally follow one another. The Nairobi sondes are higher than the SHADOZ climatology throughout the stratosphere. The JOSIE-2000 tests showed a mostly positive bias for the Meteoswiss method above 65 hPa. The Meteoswiss and NASA/WFF results appear to illustrate a difference in instrument type. The JOSIE readings shown in Figures 8c-f were taken during the same chamber simulations (Nos. 98 and 99) with identically prepared sensing solution. Relative to the OPM, the raw signal recorded with the Meteoswiss ENSCI instruments measured 5-10% more ozone throughout the simulated stratosphere than NASA/WFF with SPC. This is equivalent to an integrated ozone difference of ~20 DU, similar to the high-bias depicted for Nairobi in Figure 3a. These contrasts resemble those of the Nairobi sondes relative to the SHADOZ tropical climatology and to the Natal and Ascension offsets above ~85 hPa (compare Figures 8c and 8e). The tendency for the ENSCI instrument to record 5-7% more total ozone from 100-10 hPa than the SPC when the same solution composition and processing are employed, was a major finding of JOSIE-1998 and JOSIE-2000 [Smit and Sträter, 2004a,b]. The same behavior is observed when ENSCI and SPC instruments prepared identically are launched on the same balloon [Johnson et al., 2002; F. J. Schmidlin, personal communication, 2003]. The high ENSCI bias may explain why Watukosek is higher in the upper stratosphere than similarly prepared sondes at the three Pacific stations where the SPC instrument is used (Figure 5a)

5. Summary

In the first part of this paper total ozone columns from SHADOZ stations are compared to the new v 8 TOMS total ozone product for the period 1998-2001. At five SHADOZ sites, comparisons are also made with ground-based instruments that measure total ozone. The results can be summarized as follows:

1. Comparison of total ozone from the SHADOZ sondes and v 8 TOMS shows that, on average, the satellite records greater ozone column amount than the sondes or co-located Dobson instruments. An exception is at Paramaribo, where the sonde total ozone is more

- than 5% greater than the satellite overpass amount. These results are similar to sonde comparisons with v 7 TOMS [Thompson et al., 2003a] but there is a 1-2% improvement in agreement between the sonde ozone and v 8 TOMS due to re-calibration of TOMS.
- 2. Station-to-station total column differences between sonde and TOMS v 8 ozone, averaged from 1998-2001, are similar to those for 1998-2000 based on comparisons with TOMS version 7 [Thompson et al., 2003a]. Also similar to v 7, the worst agreement between TOMS v8 and the southern hemisphere sondes occurs at stations with the lowest tropospheric column ozone.
- 3. Evaluation of column ozone segments within the stratosphere, based on 1998-2002 SHADOZ data, shows the same stratospheric uniformity (no longitudinal wave-one) and upper stratospheric biases reported by Thompson et al. [2003a].

In the second part of our analysis, variability among SHADOZ stations, normalized to a climatological profile, is evaluated through comparison with instrument performance in JOSIE-2000 chamber simulations of balloon ascents in a tropical regime. The major findings include:

- 4. Nairobi sondes from SHADOZ show a high-ozone bias throughout the stratosphere relative to the other southern hemisphere station data. As a result, the mean stratospheric ozone column amount over Nairobi is ~15 DU higher.
- 5. The JOSIE-2000 chamber tests suggest that the high-ozone bias at Nairobi can be explained by a combination of the instrument type and sensing solution employed by the Meteoswiss-Kenya Meteorological Department. Above the 20-km mark in the JOSIE chamber, the Meteoswiss (ENSCI) instrument read 5-10% higher than the NASA/WFF instrument (SPC) that used the same solution type. Similar contrasts occur in normalized Nairobi and Ascension/Natal ozone profiles.
- 6. In JOSIE-2000 too low ozone was measured in lower stratospheric segments (100-60 hPa) where sonde responses lag the standard photometer by 20-30 seconds. This effect appears in segments of four SHADOZ stations (Ascension, Natal, Samoa, San Cristóbal).
- 7. The impact of sensing solution composition on SHADOZ station variability is harder to assess because PSCs are included in the archived data. JOSIE-2000 results show memory effects associated with buffered solutions (used at all sites except those with the NOAA/CMDL method), especially in the lowest ozone segments (~100 hPa). The memory effects may also explain positive offsets above 20 hPa at Nairobi and Natal. At Fiji, Samoa and San Cristóbal, where unbuffered solutions are used, upper stratospheric ozone profiles are lower than the SHADOZ-defined climatology.

Bearing in mind that SHADOZ statistics represent hundreds of balloon flights at some stations, compared to a small number of simulations in the JOSIE-2000 test chamber (two prototype profiles/technique), it is gratifying to note that sonde deviations in JOSIE are roughly reflected in the sonde biases within the SHADOZ dataset. Ozonesonde instrument issues will be further evaluated with results from an April 2004 balloon intercomparison called BESOS (Balloon Experiment for Standards of Ozonesondes; http://croc.gsfc.nasa.gov/besos). As in the JOSIE experiments, BESOS features a standard ozone photometer through which a set of sondes flown on the same gondola are intercompared (cf Hilsenrath et al., 1986).

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Table 1. SHADOZ sites, instrument technique, parameters during JOSIE-2000 tests.

SHADOZ Sites	Lat./Long.	. (deg)	Station Meth.	Station Instru.	JOSIE Meth.*	JOSIE Instru.
Suva, Fiji	-18.13	178.40	2% KI	SPC	2% KI	SPC
Pago Pago, Am. Samoa	-14.23	-170.56	2% KI	SPC	2% KI	SPC
Papeete, Tahiti	-18.00	-149.00	2% KI	SPC	2% KI	SPC
San Cristóbal, Galapagos	-0.92	-89.60	2% KI	SPC	2% KI	SPC
Paramaribo, Surinam	5.81	-55.2	1% KI	SPC		
Natal, Brazil	-5.42	-35.38	1% KI	SPC,** ENSCI	1 % KI	SPC
Ascension Island	-7.98	-14.42	1% KI	SPC,** ENSCI	1% KI	SPC
Irene, South Africa	-25.25.	28.22	1% KI	SPC		
Nairobi, Kenya	-1.27	36.80	1% KI	ENSCI	1% KI	ENSCI
Malindi, Kenya	-2.99	40.19	1% KI	SPC	_	
La Réunion	-21.06	55.48	.5, 1% KI	SPC,** ENSCI	.5, 2% KI	ENSCI
Watukosek, Indonesia	-7.57	112.65	1%?	ENSCI		
Kaashidhoo, Maldivest	5.0	73.5	2% KI	ENSCI		
Aerosols99 Cruise†		-	2% KI	ENSCI		

^{*} Responsible Co-I JOSIE participant: NOAA/CMDL for Fiji, Samoa, San Cristobal, Tahiti; NASA Wallops Flight Facility (WFF) for Natal, Ascension; Méteosuisse for Nairobi; Univ. Réunion for La Réunion. FZ-Juelich JOSIE participant test method used at Irene, Paramaribo.

^{**} Mixture of solution strengths, instruments used; see details in Thompson et al. [2003a]

[†] Campaign data in SHADOZ archive. 23 sondes from Aerosols99 cruise, January-February 1999 [Thompson et al., 2000]; 54 sondes from Kaashidhoo taken during late January-March 1999 [Figure 11b in Thompson et al., 2003b]

Table 3. Ozone summary from 1998-2002 SHADOZ data. Total sample number given along with the number of profiles to 10 hPa, on which statistics are based.

Site	Sample No. Aotal profiles	Integrated O ₃ , 10	Trop O ₃ , 10	Int. O ₃ -Trop O ₃ , 10	CMR Add-on, 10	SBUV Add- on, 10	Total Sonde O, + CMR, 10	Total Sonde O ₃ + SBUV,	(CMR- SBUV), 10
								10	
Ascension	164/222	204.3, 21.4	37.0, 8.9	167.3, 16.2	66.2, 12.0	48.4, 7.7	270.4, 25.5	252.7, 19.7	17.7, 8.3
Fiji	151/181	202.1, 15.8	22.4, 7.5	179.7, 12.0	50.1, 8.7	38.6, 6.4	252.3, 16.5	240.8, 14.8	11.5, 5.2
Irene	100/123	224.0, 20.1	33.1, 6.0	190.9, 17.9	50.0, 10.0	39.9, 7.1	274.0, 22.6	263.9, 19.4	10.2, 5.9
Watokusek	82/140	208.4, 16.7	24.4, 7.2	184.0, 14.3	55.1, 11.8	37.7, 6.7	263.4, 22.3	246.1, 14.3	17.3, 10.6
Malindi	45/67	219.6, 32.3	32.4, 6.3	191.6, 12.6	57.5, 14.0	38.1, 7.6	277.1, 39.3	257.8, 32.0	19.3, 9.4
Nairobi	193/231	221.6, 14.4	28.8, 5.4	192.7, 12.4	59.4, 10.3	39.3, 6.8	281.0, 14.4	260.9, 12.3	20.1, 5.9
Natal	150/177	214.3, 17.4	32.9, 8.5	181.4, 13.7	65.1, 12.1	44.0, 7.8	279.4, 22.8	258.3, 17.3	21.1, 8.4
Paramaribo	125/156	236.0, 15.8	39.8, 87.0	196.3, 88.2	64.9, 11.6	40.9, 7.0	300.9, 18.0	276.9, 13.4	24.0, 8.1
Reunion	95/149	210.0, 17.7	32.8, 7.4	177.1, 14.1	56.6, 10.9	43.1, 8.1	266.6, 20.0	253.1, 15.5	13.5, 8.5
Samoa	162/194	201.0, 12.9	19.8, 5.9	181.2, 9.8	51.0, 8.3	36.1, 4.5	252.0, 15.0	237.1, 12.3	14.8, 5.7
San Cristobal	191/217	200.4, 14.3	23.6, 4.5	176.8, 12.3	49.3, 9.5	37.3, 5.8	249.7, 16.3	237.7, 12.7	12.0, 6.9

calibration performed by the station Co-Investigator, who may re-process at any time. Updates (with most recent processing date) are given on the Total samples used in statistical analyses (first column): 1458. The SHADOZ project archives data in a uniform format, with initial analysis and website. Some sites report data every 10 seconds during a flight, whereas other profiles are archived with 1-s frequency. Data from SHADOZ stations maintained at other archives may differ from SHADOZ in format, ozone integration and extrapolation.

REFERENCES

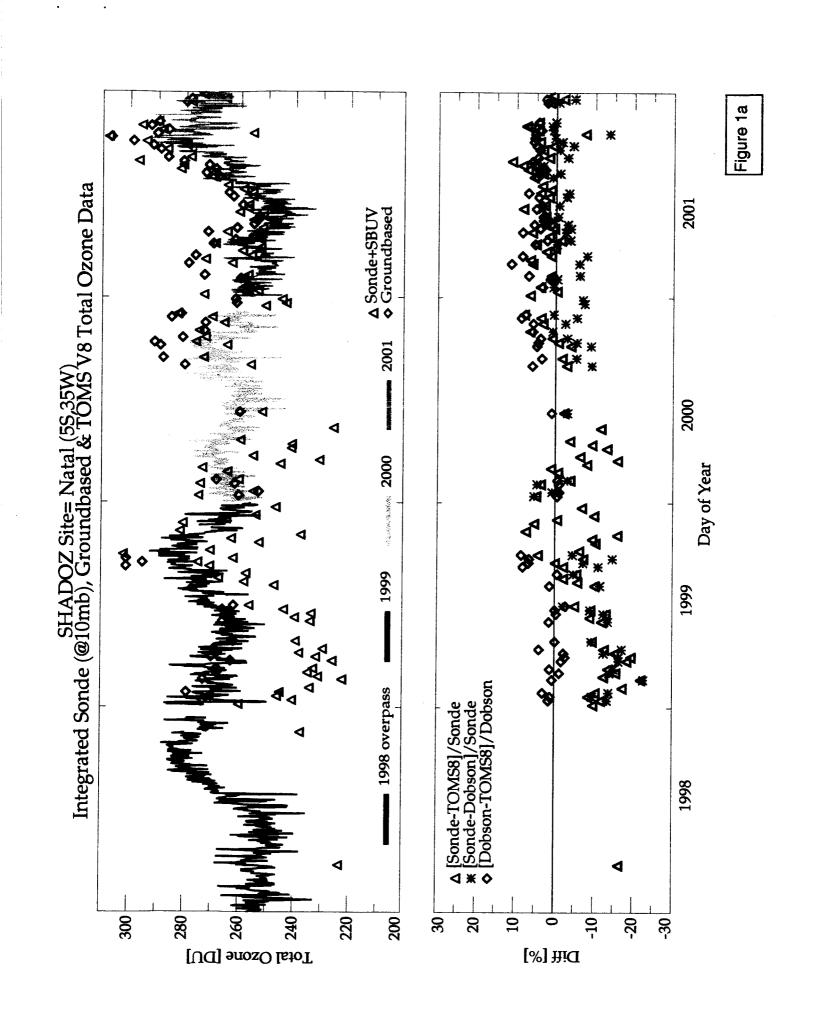
- Bodeker, G. E., J. C. Scott, K. Kreher, and R. L. McKenzie, Global ozone trends in potential vorticity coordinates using TOMS and GOME intercompared against the Dobson network: 1978-1998, J. Geophys. Res., 106, 23029-23042, 2001.
- Chatfield, R. B., H. Guan, A. M. Thompson, and J. C. Witte, Convective lofting links Indian Ocean air pollution to paradoxical south Atlantic ozone maxima, *Geophys. Res. Lett.*, 31, L06103, doi: 10.129/2003GL016688, 2004.
- Edwards, D. P., et al., Tropospheric ozone over the Atlantic: A satellite perspective, J. Geophys. Res., 108, 4237, doi: 10.129/2002JD002927, 2003.
- Fishman, J. and A. Balok, Calculation of daily tropospheric ozone residuals using TOMS and empirically improved SBUV measurements: Application to an ozone pollution episode over the eastern United States, J. Geophys. Res., 104, 30319-30340, 1999.
- Fishman, J., and J. C. Larsen, Distribution of total ozone and stratospheric ozone in the tropics Implications for the distribution of tropospheric ozone, J. Geophys. Res., 92, 6627-6634, 1987.
- Hilsenrath, E., et al., Results from the Balloon Ozone Intercomparison Campaign (BOIC), J. Geophys. Res., 91, 13137-13152, 1986.
- Hudson, R. D., J. Kim, and A. M. Thompson, On the derivation of tropospheric column ozone from radiances measured by the Total Ozone Mapping Spectrometer, J. Geophys. Res., 100, 11138-11145, 1995.
- Jenkins, G. S., J-H. Ryu, A. M. Thompson, J. C. Witte, Linking horizontal and vertical transport of biomass fire emissions to the tropical Atlantic ozone paradox during the Northern Hemisphere winter season. 1999, J. Geophys. Res., 108, 4745, doi:10.129/2002JD003297, 2003.
- Johnson, B. J., S. J. Oltmans, H. Vömel, T. Deshler, C. Kroger and H. G. J. Smit, ECC ozonesonde pump efficiency measurements and sensitivity tests of buffered and unbuffered sensor solutions, J. Geophys. Res. 107, D19, 4393, doi: 10.129/2001JD000557, 2002.
- Komhyr, W. D., Nonreactive gas sampling pump, Rev. Sci. Inst., 38, 981-983, 1967.
- Komhyr, W. D., Operations Handbook Ozone measurements to 40 km altitude with model 4A-ECC-ozone sondes, NOAA Techn. Memorandum ERL-ARL-149, 1986.
- Komhyr, W. D., R. A. Barnes, G. B. Brothers, J. A. Lathrop, and D. P. Opperman, Electrochemical concentration cell ozonesonde performance during STOIC, *J. Geophys. Res.*, 100, 9231-9244, 1995.
- Logan, J.A., Trends in the vertical distribution of ozone: An analysis of ozone sonde data, J. Geophys. Res., 99, 25553 25585, 1994.
- Logan, J. A., D. B. A. Jones, I. A. Megretskaia, W. Randel, S. J. Oltmans, B. J. Johnson, H. Voemel, W. Kimani, and F. J. Schmidlin, The quasi-biennial oscillation in equatorial ozone as revealed by ozonesonde and satellite data, *J. Geophys. Res.*, 108, doi: 10.129/2002JD002170, 2003.
- McPeters, R. D., G. J. Labow and B. J. Johnson, A satellite-derived ozone climatology for balloonsonde estimation of total column ozone, *J. Geophys. Res.*, 102, 8875-8885, 1997.
- Newchurch, M. J., D. Sun and J-J. Kim, Zonal wave-1 structure in TOMS tropical stratospheric ozone, *Geophys. Res. Lett.*, 28, 3151-3154, 2001.
- Peters, W., M. C. Krol, J. P. F. Fortuin, H. M. Kelder, C. R. Becker, A. M. Thompson, J. Lelieveld, P. J. Crutzen, Tropospheric ozone over a tropical Atlantic station in the northern hemisphere: Paramaribo, Surinam (6N, 55W), *Tellus B*, **56**, 21-34, 2004.
- Shiotani, M. Annual, quasi-biennial and El Nino-Southern Oscillation (ENSO) time-scale variations in Equatorial total ozone, J. Geophys. Res., 97, 7625-7634, 1992.
- Shiotani, M., and F. Hasebe, Stratospheric ozone variations in the equatorial region as seen in Stratospheric Aerosol and Gas Experiment data, J. Geophys. Res., 99, 14575-14584, 1994.
- Smit, H. G. J., W. Sträter, M. Helten, and D. Kley, Environmental simulation facility to calibrate airborne ozone and humidity sensors, Jülich Berichte Nr 3796, Forschungszentrum Jülich, 2000.
- Smit, H. G. J., and W. Sträter, JOSIE-1998: Performance of ECC Ozone Sondes of SPC-6A and ENSCI-A Type, in WMO Global Atmospheric Watch Report Series (Technical Document), World Meteorological Organization, Geneva, in press, 2004a.
- Smit, H. G. J., and W. Sträter, JOSIE-2000: The 2000 WMO international intercomparison of operating procedures for ECC-sondes at the environmental simulation facility at Jülich, in WMO Global Atmospheric Watch Report Series (Technical Document), World Meteorological Organization, Geneva, in press, 2004b.
- Thompson, A. M. and R. D. Hudson, Tropical tropospheric ozone (TTO) Maps from Nimbus 7 and Earth-Probe TOMS by the modified-residual method: Evaluation with sondes, ENSO signals and trends from Atlantic regional time series, J. Geophys. Res., 104, 26961-26975, 1999.
- Thompson, A. M., B. G. Doddridge, J. C. Witte, R. D. Hudson, W. T. Luke, J. E. Johnson, B. J. Johnson, S. J. Oltmans, and R. Weller, A tropical Atlantic ozone paradox: Shipboard and satellite views of a tropospheric ozone

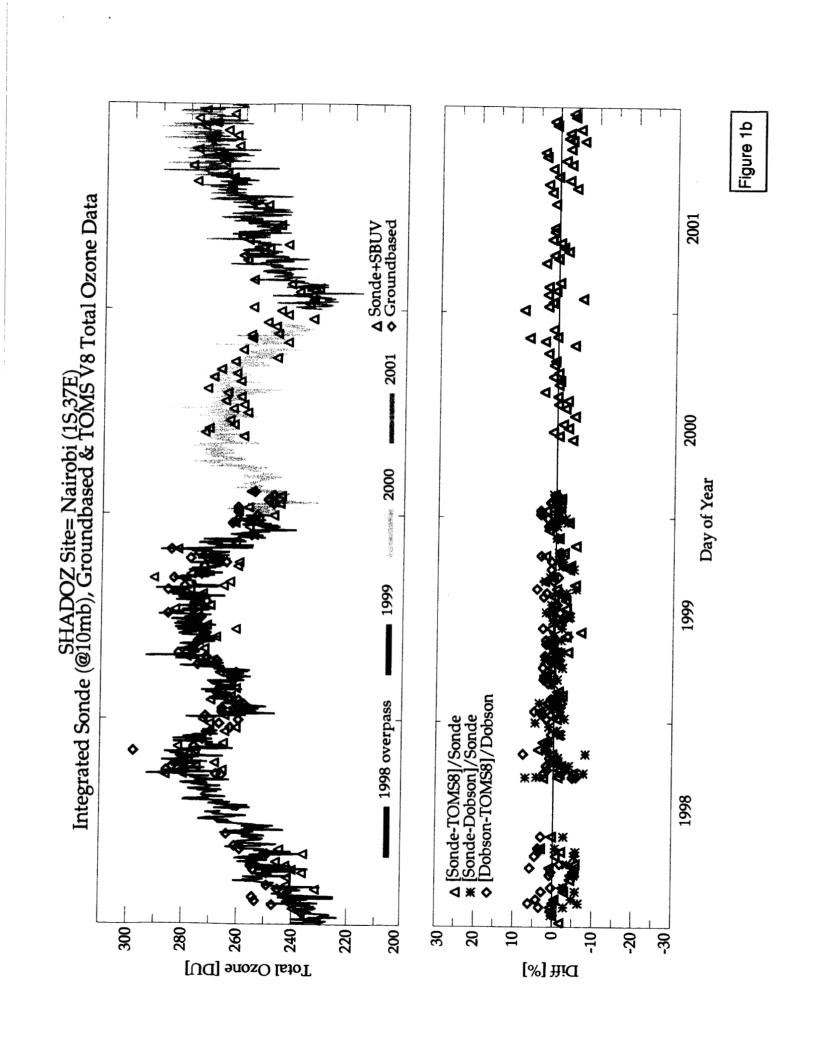
- maximum and wave-one in January-February 1999, Geophys. Res. Lett., 27, 3317-3320, 2000.
- Thompson, A. M., et al., Southern Hemisphere Additional Ozonesondes (SHADOZ) 1998-2000 tropical ozone climatology. 1. Comparison with TOMS and ground-based measurements, J. Geophys. Res., 108, D2, 8238, doi: 10.129/2001JD000967, 2003a.
- Thompson, A. M., et al., Southern Hemisphere Additional Ozonesondes (SHADOZ) 1998-2000 tropical ozone climatology. 2. Tropospheric ozone variability and the zonal wave-one, *J. Geophys. Res.*, **108**, D2, 8241, doi: 10.129/2002JD002241, 2003b.
- WMO (World Meteorological Organization), SPARC/IOC/GAW Assessment of Trends in the Vertical Distribution of Ozone, ed. By N. Harris, R. Hudson and C. Phillips, SPARC Report No. 1, WMO Global Ozone Research and Monitoring Project, Report No. 43, Geneva, 1998a.
- WMO (World Meteorological Organization), JOSIE, ed. by H. Smit and D. Kley, Report No. 130, WMO Global Ozone Research and Monitoring Project, Report No. TD926, Geneva, 1998b.
- Ziemke, J. R., S. Chandra, and P. K. Bhartia, Two new methods for deriving tropospheric column ozone from TOMS measurements: The assimilated UARS MLS/HALOE and convective-cloud differential techniques, J. Geophys. Res., 103, 22115-22128, 1998.
- Ziemke, J. R., S. Chandra, and P. K. Bhartia, Upper tropospheric ozone derived from the cloud slicing technique: Identification of the regional aspects of air pollution, J. Geophys. Res., 108, 4390, doi: 10.129/, 2002.

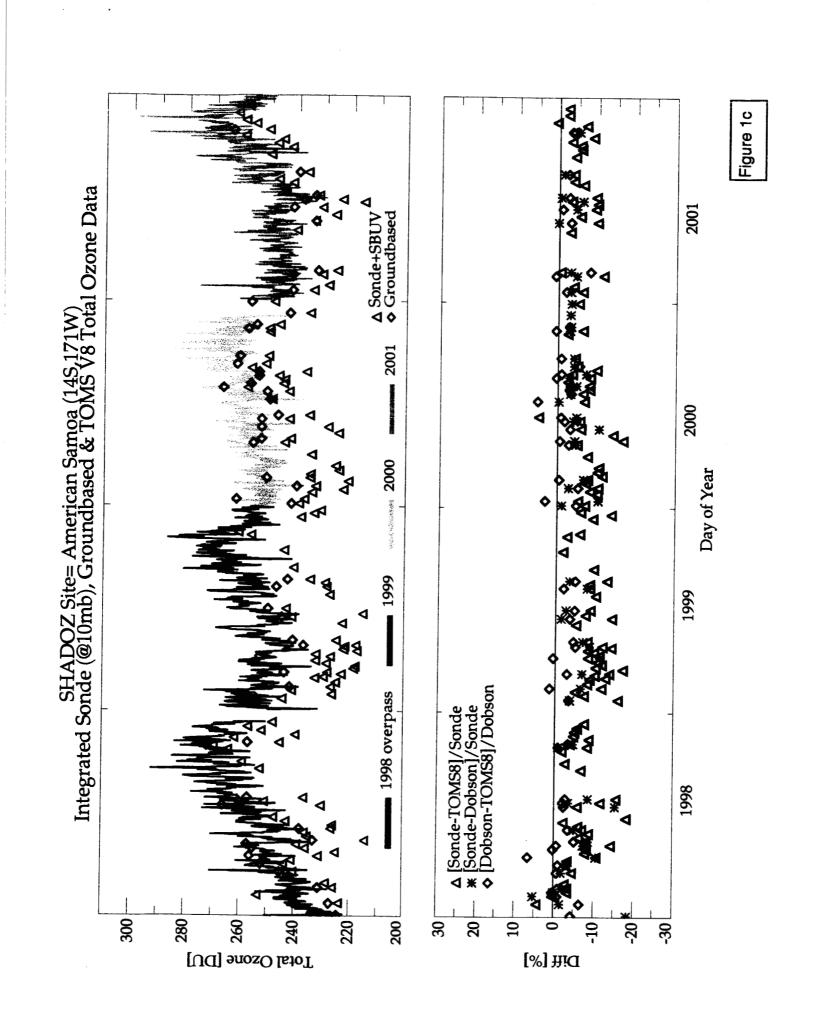
Figure Captions

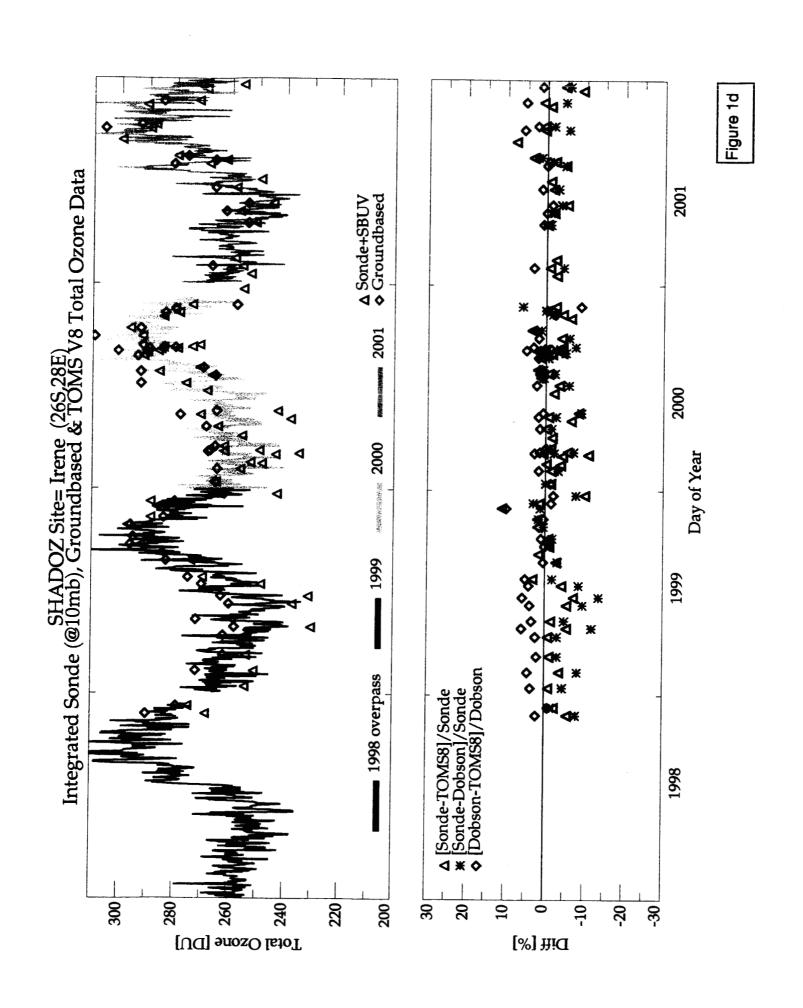
- Fig 1 Upper Panel: A comparison of integrated total ozone from sondes, TOMS satellite (Level 2, version 8) overpasses and Dobson or Brewer instruments at the following SHADOZ stations:
 (a) Natal; (b) Nairobi; (c) Irene; (d) Samoa; (e) Paramaribo. Lower Panel: % deviation relative to the sonde or the ground-based instrument (TOMS version 8). Sonde-ground-based instrument differences are indicated by a *. Integrated ozone from sondes based on data to 10 hPa with extrapolation above 10 hPa from McPeters et al. [1997] climatology. In Thompson et al. [2003a], comparisons are with TOMS v 7 total ozone and sondes reaching 7 hPa before balloon burst. Overall features using v 7 resemble those shown here with v 8.
- Fig 2 Summary of averaged differences between total ozone from SHADOZ sondes and from TOMS (v 7; cf Figure 9, Thompson et al., 2003a) and sondes and TOMS v 8. Data to 10 hPa (Table 3) with SBUV extrapolation are used for sonde total ozone. Shaded region corresponds to "best total ozone" based on Dobsons and most recent TOMS calibration.
- Fig 3 (a) Zonal view of stratospheric column ozone determined from integrated stratospheric ozone of soundings plus SBUV extrapolation. Bars indicate 1-σ standard deviation. For Irene, column may be higher because mid-latitude stratospheric conditions often prevail. The lack of distinct zonal variation in the stratospheric column signifies the absence of a zonal wave-one in the stratosphere. However, uncertainty about the tropopause location introduces 4-5 DU imprecision in the values shown and a wave amplitude smaller than that could not be verified; (b) zonal view of integrated column ozone (DU) between 15 and 20 km, with 1-σ standard deviation; (c) zonal view of the difference between average CMR (constant-mixing-ratio) extrapolations and SBUV for SHADOZ stations.
- Fig 4 Summary of averaged differences between total ozone from SHADOZ sondes and from TOMS (*, v 8, as in Fig 2) with difference between co-located ground-based total ozone and TOMS (□, v 8). Also shown for each station is the mean difference in total ozone between the representative JOSIE-2000 sonde type and the JOSIE-2000 chamber standard (♦, standard = OPM, ozone photometer).
- Fig 5 Mean ozone profiles (from 1998-2002) from soundings that reached 7.0 hPa pressure based on 0.25 km averages. (a) Pacific, eastern Indian Ocean stations: Fiji, American Samoa, San Cristóbal, Watukosek; (b) Atlantic and Kenyan sites: Natal (Brazil), Ascension, Nairobi, Malindi; (c) two sub-tropical stations in SHADOZ, Réunion and Irene. The standard deviation (1-σ) for these averages is +/-1.5 mPa at the stratospheric maximum and ~0.3 mPa elsewhere in the stratosphere. In the middle troposphere, due to large natural variability, the 1-σ standard deviation is ~0.5 mPa at the Pacific stations and > 1 mPa at the others. Constant-

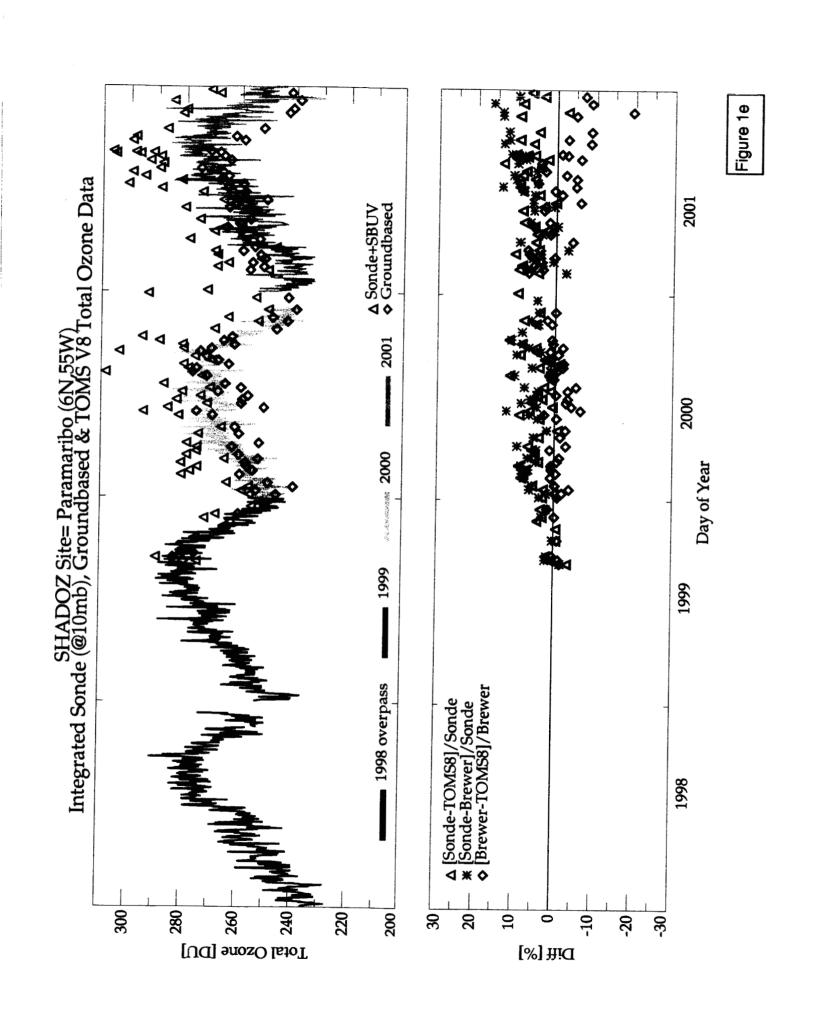
- mixing ratio (CMR) isolines are also illustrated. Our CMR definition uses the uppermost measured points before 7 hPa, then adds a column amount up to 1 hPa. The corresponding mean CMR above 7.0 hPa is given in Table 3.
- Fig 6 Climatological mean profiles based on 1998-2002 SHADOZ data with mean and 1-σ standard deviation (shaded). (a) "tropical" based on all southern hemisphere SHADOZ stations except Réunion and Irene; (b) "sub-tropical" based on Réunion and Irene data. Constant mixing ratio isolines shown.
- Fig 7 Mean SHADOZ station profiles (1998-2002) shown in Figure 5a,b normalized to the climatological mean in Figure 6a. (a) Samoa; (b) San Cristóbal; (c) Fiji; (d) Ascension; (e) Natal; (f) Nairobi; (g) Malindi; (h) Watukosek.
- Fig 8 Same deviations as Figure 7 except stratospheric portion of sonde illustrated from 100-10 hPa. Stations are clustered according to technique used. Also shown are deviations of participant specified corrections (PSC) from OPM standard in JOSIE-2000. (a,b) NOAA/CMDL JOSIE with deviations from SHADOZ tropical mean profile for Samoa, Fiji, San Cristóbal; (c,d) NASA/WFF JOSIE deviations with SHADOZ deviations based on Natal and Ascension data; (e,f) Meteoswiss JOSIE deviations with Nairobi deviation from SHADOZ tropical mean. JOSIE-2000 data are two minute running averages.











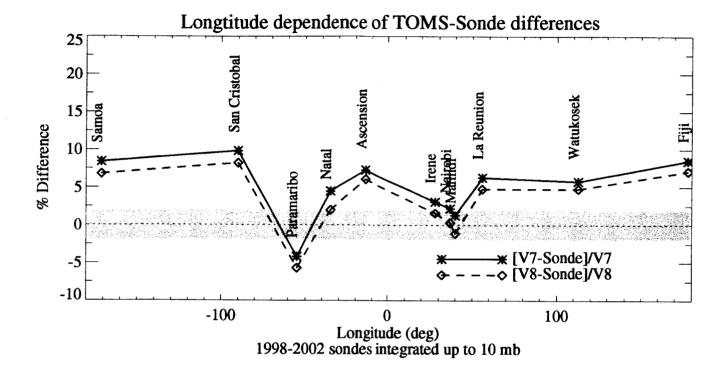


Figure 2

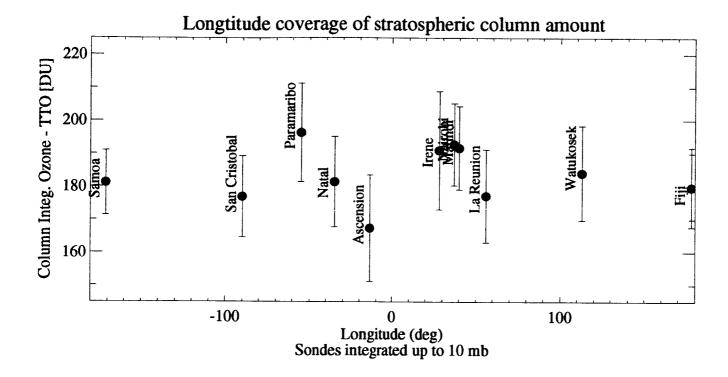


Figure 3a

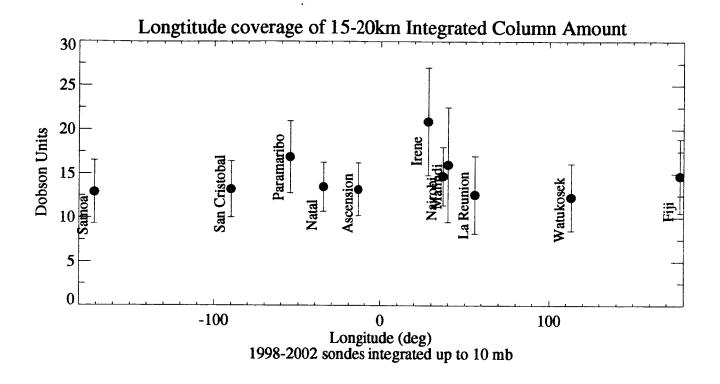


Figure 3b

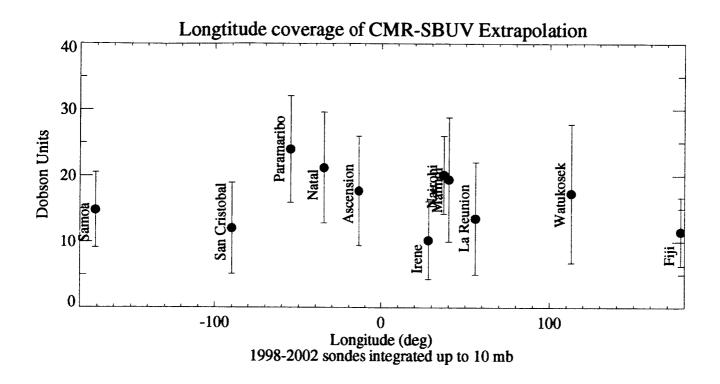


Figure 3c

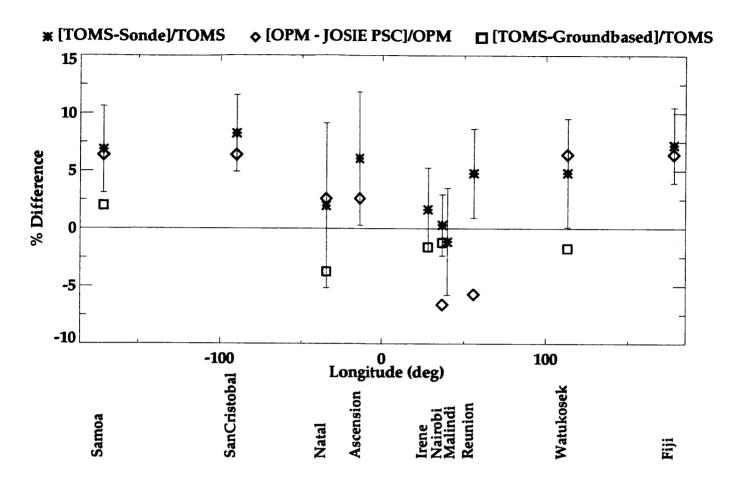


Figure 4

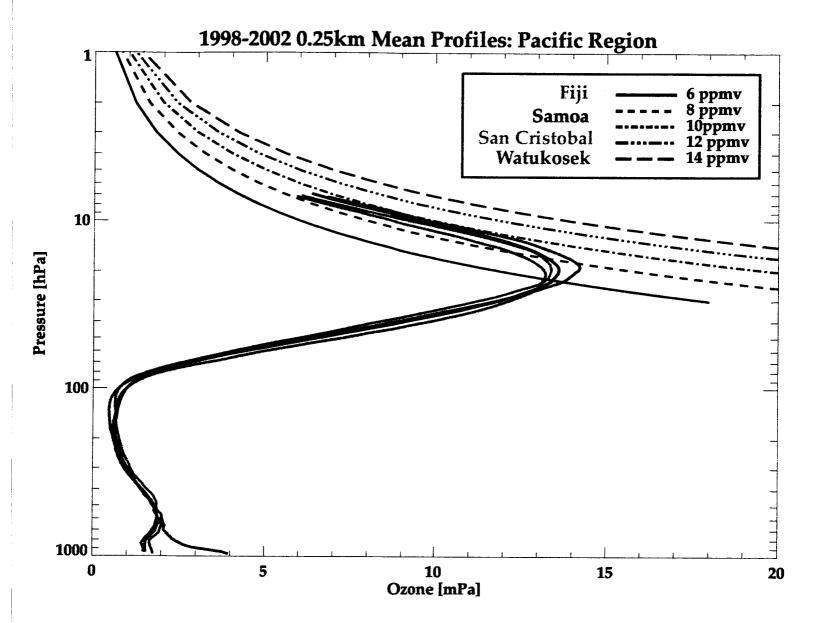


Figure 5a

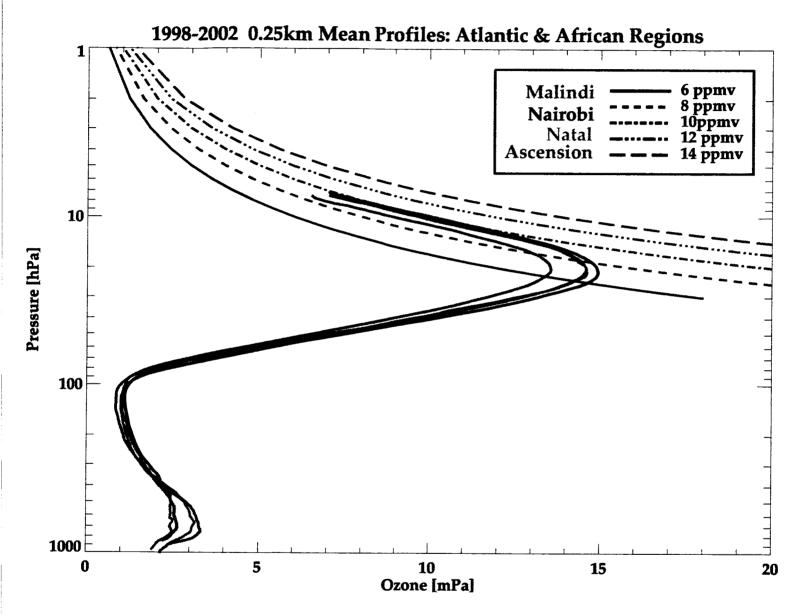


Figure 5b

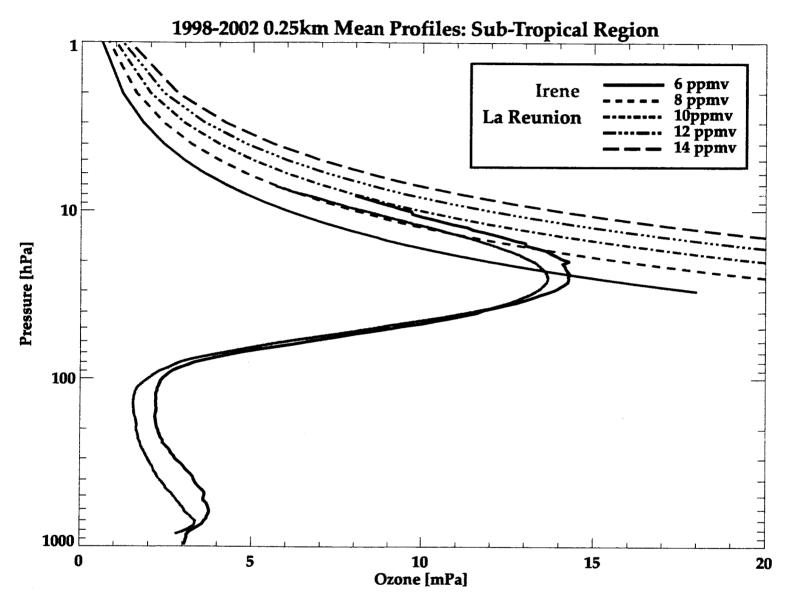
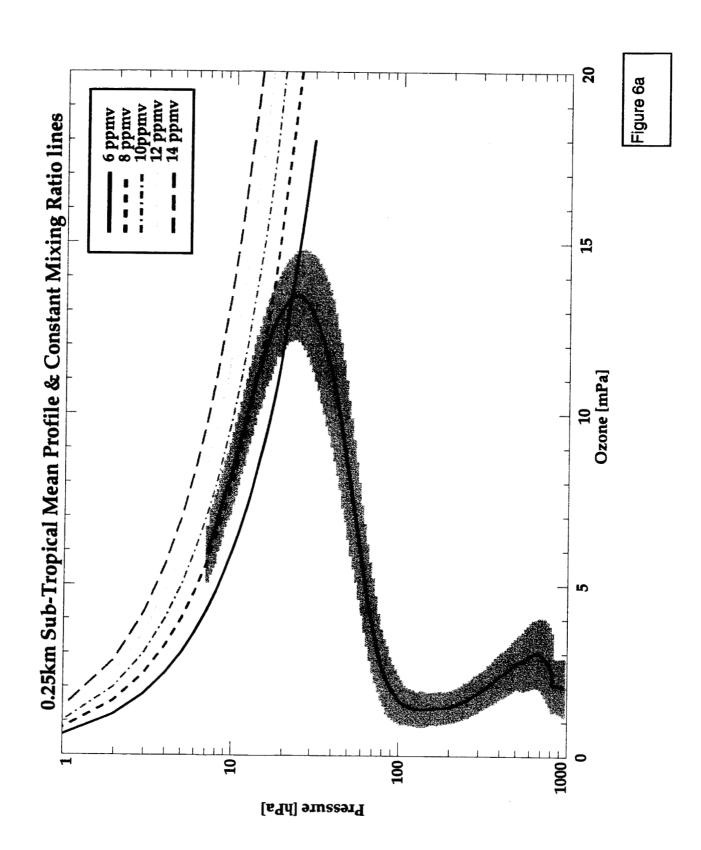
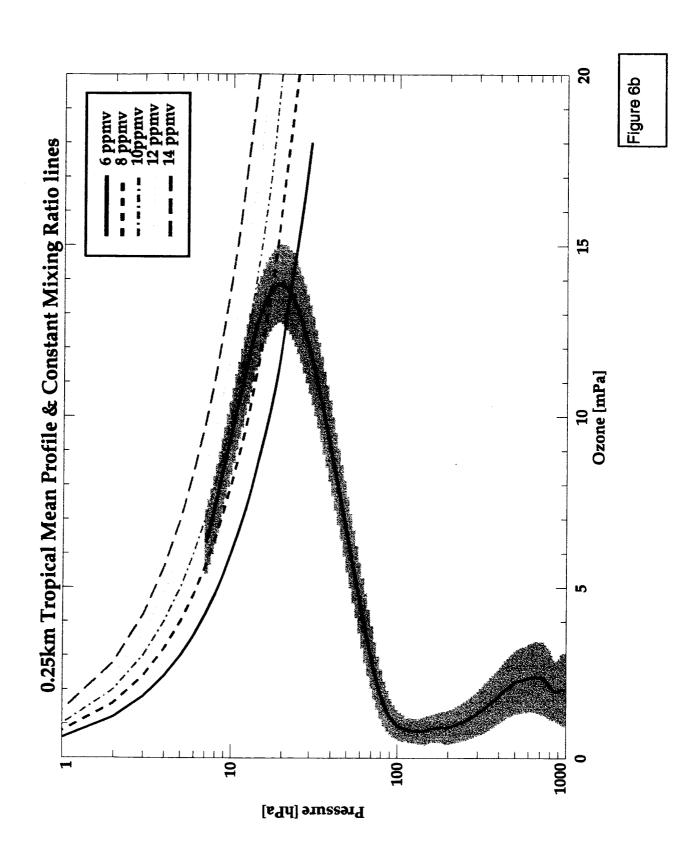


Figure 5c





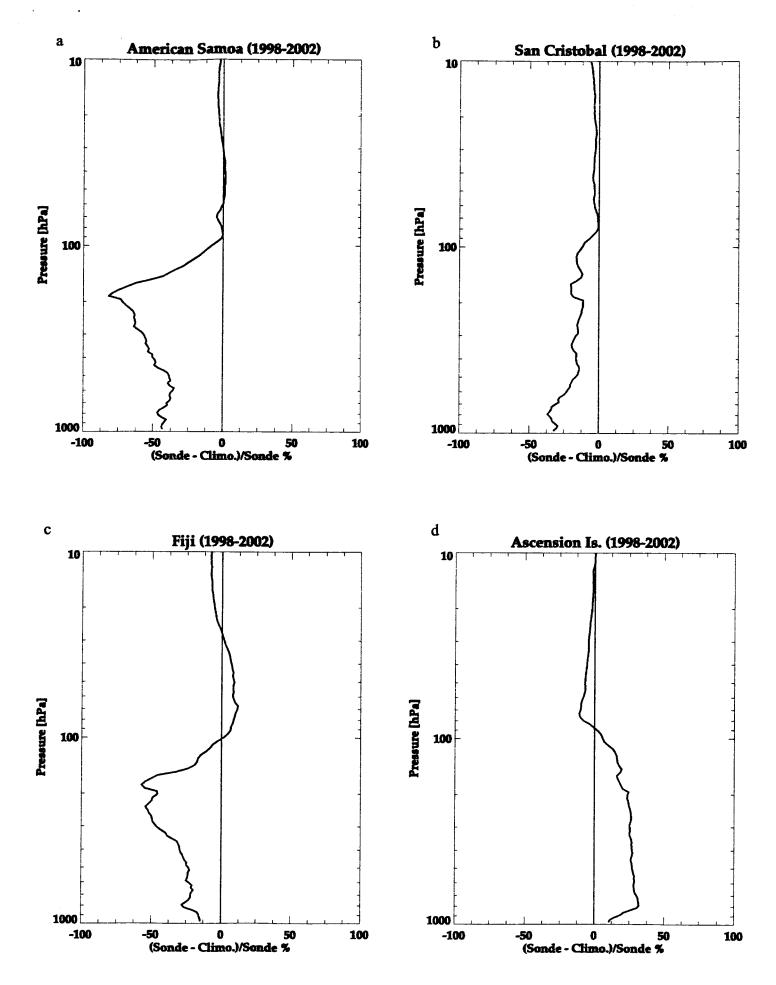
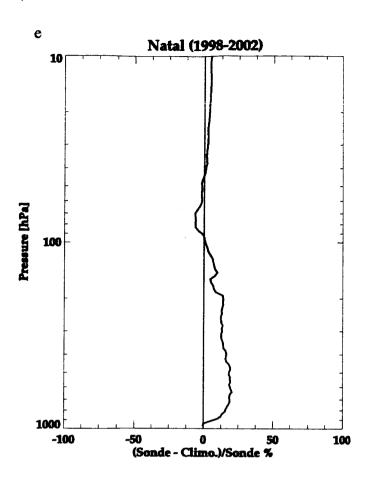
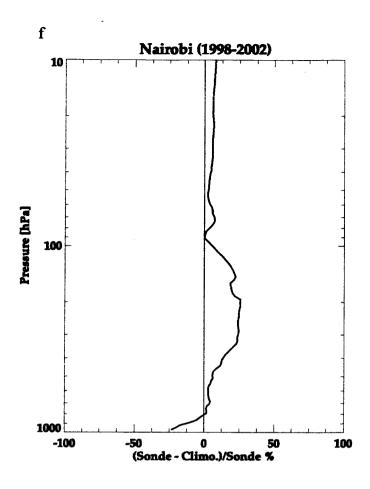
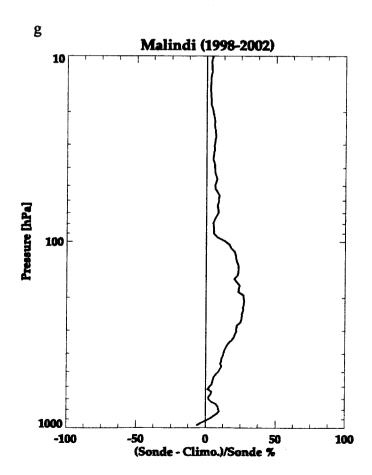


Figure 7







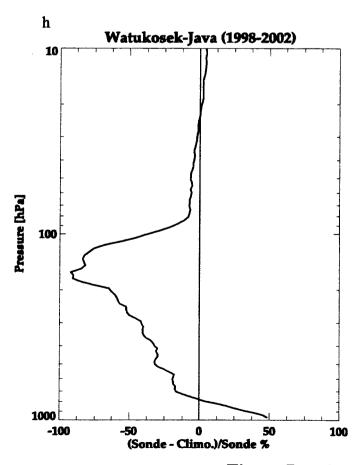
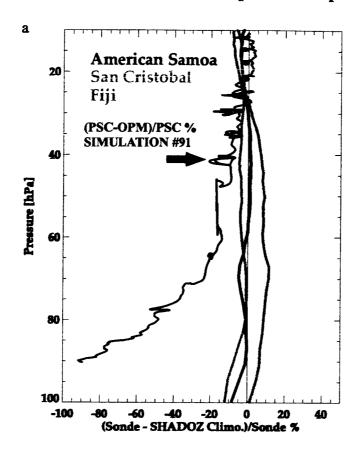


Figure 7 con't

1998-2002 SHADOZ/JOSIE profile comparisons



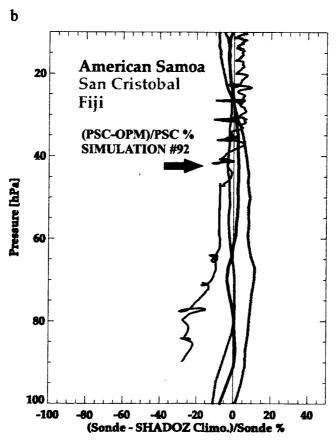
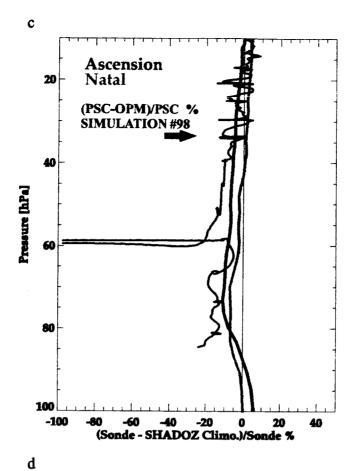


Figure 8



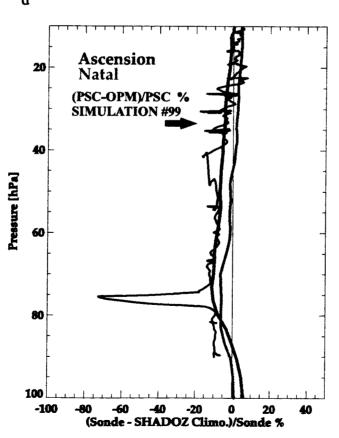


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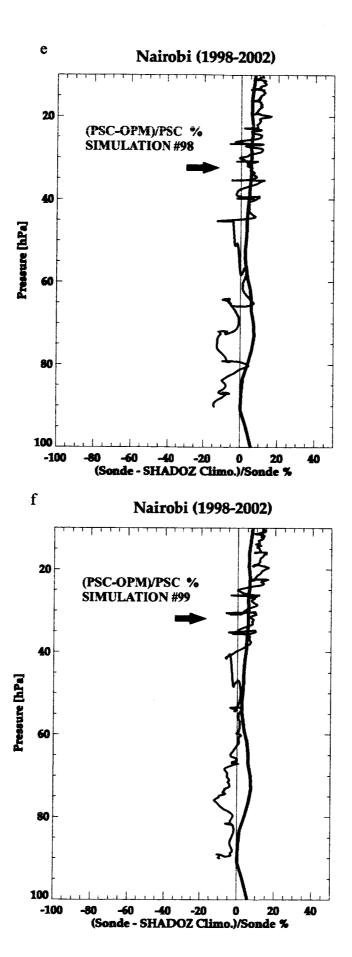


Figure 8 con'd

Popular Summary

The Southern Hemisphere Additional Ozonesondes (SHADOZ) 1998-2002 Tropical Ozone Climatology. 3. Instrumentation and Station-to-station Variability

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Since 1998 the Southern Hemisphere Additional OZonesondes (SHADOZ) project has collected more than 2000 ozone profiles from a dozen tropical and subtropical sites using balloon-borne electrochemical concentration cell (ECC) ozonesondes. See: <http://croc.gsfc.nasa.gov/shadoz>. It turns out that analysis of ozonesondes data from SHADOZ [Thompson et al., 2003a] revealed that variations in ozonesonde technique might cause station-to-station biases in the ozone readings. In Sept 2000 we had an opportunity to participate in the JOSIE-2000 chamber tests with all the SHADOZ methods mentioned. The purpose was to examine SHADOZ data in the light of the chamber tests. We found that certain variations in SHADOZ ozone profiles are accounted for by differences in solution composition, data processing and instrument (manufacturer). Instrument bias leads to a greater ozone measurement above 25 km over Nairobi and to lower total column ozone at three Pacific sites compared to other SHADOZ stations at 0-20°S. in the measurements. We also in this paper compared SHADOZ total ozone column amounts to version 8 TOMS (2004 release). Discrepancies between sonde and satellite datasets declined 1-2 percentage points on average, compared to version 7 TOMS but were still quite at variance (up to 8%) in total ozone at some sites.